Supporting Information

Unpredicted but it exists: trigonal Sc₂Ru with a significant metal-metal charge transfer

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Supporting information

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Experiment vs. high-throughput data.

A comparison between experimental data and high-throughput first principles calculation results is illustrated in Figure S1 for the Sc-Ru system. In general, there is a good correlation between them except the cases indicated by red numbers for which, according to high-throughput data:

1) the Sc₅Ru₃ is unstable at low temperatures;
2) the experimentally obtained Sc₂Ru (hP96-Ti₂Ni) is far away from the decomposition line: there are several 2:1 stoichiometry structural models (including the ground state tI₆-Mo₂Si) that possess noticeably lower formation energies;
3) the Sc₅₇Ru₁₃ is slightly unstable at low temperatures.

Figure S1. Sc-Ru convex-hull taken from [http://www.aflow.org/aflow-chull](http://www.aflow.org/aflow-chull) implemented within the opensource, ab initio framework [http://www.aflow.org](http://www.aflow.org). Red markers indicate discrepancies between experimental and high-throughput data.
**Synthesis and SEM-EDXS characterisation**

Stoichiometric amounts of Ru and Sc, with nominal purities > 99.9 mass% were used for synthesis of an alloy of ca. 0.8 g. The sample was arc melted several times under Ar atmosphere on a water-cooled copper hearth with a tungsten electrode; weight losses were less than 1 mass%. Subsequently, the obtained alloy was put in an alumina crucible, sealed in a silica tube under Ar atmosphere and heat treated at 1000 °C for 7 days. Annealing was followed by water quenching. In order to obtain smooth surfaces suitable for microscopic analysis, some specimen fragments were embedded in a phenolic hot mounting resin with carbon filler, employing an automatic hot compression mounting press Opal 410 (ATM GmbH, Germany). The grinding procedure with abrasive SiC papers (grain size from 600 to 1200) was followed by diamond pastes (6, 3 and 1 μm) polishing. Microstructure examination (see Figure S2) and phase composition analyses were performed by a scanning electron microscope (SEM) Zeiss Evo 40 equipped with an Energy Dispersive X-ray (EDX) Spectroscope Oxford Instruments INCA X-ACT operated by the INCA Energy software (Oxford Instruments, Analytical Ltd., Bucks, U.K.). Calibration for the elemental analysis was performed on a cobalt standard.

![Figure S2.](image)

**X-ray studies and crystal structure solution**

The single crystal selection was conducted on the mechanically fragmented alloy. X-ray diffraction measurements were performed by a Bruker Kappa APEXII CCD area-detector diffractometer, using Mo Kα (λ = 0.71073 Å) radiation. Datasets were collected operating in ω-scan mode over the reciprocal space up to θ ≈ 30°, with an exposure time of 30 seconds per frame. The crystal-to-detector distance was fixed to 5 cm. Data integration, Lorentz polarization, and semiempirical absorption corrections were applied to all data by using the SAINT and SADABS softwares. Crystal structure refinement was carried out by full-matrix least-squares methods on |F|^2 using the SHELXL program as implemented in WinGX. The indexation of collected intensity data yielded
to a trigonal symmetry unit cell with $a=9.35$ Å and $c=11.29$ Å (precession images of $h0l$ and $hk0$ zones are shown in Fig. S3).

![Figure S3. Reconstructed intensity profiles for $h0l$ (a) and $hk0$ (b) zones of the Sc$_2$Ru diffraction pattern.](image)

Since no systematic absences were found, the following space-groups were suggested by XPREP$^1$: $P3$ (143), $P$–$3$ (147), $P321$ (150), $P3m1$ (156), $P$–$3m1$ (164). The lowest combined figure of merit was associated to the last one. Indeed, the crystal structure was quickly solved in this space-group by means of the charge-flipping algorithm implemented in JANA2006$^4$ figuring out the almost complete structural model with 45 atoms per cell (5 Ru and 7 Sc Wyckoff sites). Site occupancy factors (SOF) and possible statistical mixture were carefully checked for each species in separate refinement cycles, but no significant deviation from an ordered scenario was detected, suggesting Sc$_2$Ru to be a stoichiometric compound. This is also in perfect agreement with the measured EDXS composition. A further refinement including anisotropic thermal displacement parameters resulted in acceptable residuals and flat difference Fourier map (Table S1). The generated CIF file has been deposited at Cambridge Crystallographic Data Centre (code-2071469). Details of the data collection and refinement are listed in Table S1. Interatomic distances for Sc$_2$Ru ($hP45$) - in Table S2 and constructed histograms are shown in Figure S4.
Table S1. Crystallographic data for the Sc₂Ru single crystal together with some experimental details on its structure determination.

| Empirical Formula | Sc₂Ru | Calc. density [g·cm⁻³] | 5.56 |
|-------------------|-------|------------------------|------|
| EDXS composition  | Sc₀.₉Ru₃₄.₁ | Abs. coeff. [µ, mm⁻¹] | 11.85 |
| Depositing CSD-code | 2071469 | Unique reflections | 1096 |
| Structure type    | Sc₂Ru | Reflections (I > 2σ(I)) | 1010 |
| Space group       | P₃₁m | Data/parameters | 1096/54 |
| Pearson symbol, Z | hP₄₅, 15 | GOF | 1.165 |
| Unit cell dimensions: | | Rᵣᵣ/Rₛ | 0.0223/0.0089 |
| a [Å]             | 9.3583(9) | Rᵣᵣ/Rₛ (I > 2σ(I)) | 0.0134/0.0330 |
| c [Å]             | 11.285(1) | Rᵣᵣ/Rₛ (all data) | 0.0163/0.0346 |
| V [Å³]            | 855.9(2) | Δρᵣᵣ (max/min) [e/Å³] | 0.93/-1.18 |

Table S2. Interatomic distances (< 4.00 Å) for Sc₂Ru.

| Central atom | Adjacent atoms | d (Å) | Central atom | Adjacent atoms | d (Å) | Central atom | Adjacent atoms | d (Å) |
|--------------|----------------|-------|--------------|----------------|-------|--------------|----------------|-------|
| Sc1          | Ru5            | 2.6911(6) | Sc4          | Ru3 (2x)       | 2.6619(3) | Ru1          | Sc7            | 2.6623(3) |
|              | Sc4 (2x)       | 3.0248(5) |              |                |       |              |                |       |
|              | Sc7            | 3.0660(1) |              |                |       |              |                |       |
|              | Sc4            | 3.0924(8) |              |                |       |              |                |       |
|              | Ru1 (2x)       | 3.1178(4) |              |                |       |              |                |       |
|              | Sc2            | 3.2594(7) |              |                |       |              |                |       |
|              | Sc3 (2x)       | 3.2849(7) |              |                |       |              |                |       |
|              | Sc5            | 3.3615(6) |              |                |       |              |                |       |
|              | Ru3 (2x)       | 3.5136(6) |              |                |       |              |                |       |
|              | Sc1 (2x)       | 3.5884(6) |              |                |       |              |                |       |
|              | Ru4            | 3.9920(6) |              |                |       |              |                |       |
|              | Sc2            | 3.7044(5) |              |                |       |              |                |       |
|              | Ru1            | 3.7242(5) |              |                |       |              |                |       |
|              | Ru2 (2x)       | 3.7290(3) |              |                |       |              |                |       |
|              | Ru1 (2x)       | 3.0098(6) |              |                |       |              |                |       |
|              | Sc7            | 3.0117(6) |              |                |       |              |                |       |
|              | Sc3 (2x)       | 3.1697(5) |              |                |       |              |                |       |
|              | Sc6            | 3.1724(7) |              |                |       |              |                |       |
|              | Sc2            | 3.2572(7) |              |                |       |              |                |       |
|              | Sc2            | 3.2573(4) |              |                |       |              |                |       |
|              | Sc1            | 3.2594(7) |              |                |       |              |                |       |
|              | Sc7            | 3.7645(8) |              |                |       |              |                |       |
|              | Ru2            | 2.6479(5) |              |                |       |              |                |       |
|              | Ru4            | 2.7354(4) |              |                |       |              |                |       |
|              | Ru1 (2x)       | 2.8775(3) |              |                |       |              |                |       |
|              | Ru3            | 3.0001(5) |              |                |       |              |                |       |
|              | Sc5            | 3.1032(6) |              |                |       |              |                |       |
|              | Sc4 (2x)       | 3.1667(7) |              |                |       |              |                |       |
|              | Sc2 (2x)       | 3.1697(6) |              |                |       |              |                |       |
|              | Sc6            | 3.1979(6) |              |                |       |              |                |       |
|              | Sc1 (2x)       | 3.2849(4) |              |                |       |              |                |       |
Figure S4. Number of atoms \( (n) \) surrounding the Ru species as a function of the reduced distance \( d/d_{\text{min}} \). Green and blue bars indicate Sc and Ru, respectively.

Figure S5. Comparison between experimental (black line) and theoretical diffraction patterns: Sc$_2$Ru (red line) and Sc$_{11}$Ru$_4$ (blue line, minor quantity). Inset shows a zoom of the 15–50° range of the pattern.
The X-ray powder diffraction pattern was collected using a Philips X'Pert MPD (Cu $K\alpha$ radiation, scanning step ca. 0.015°) diffractometer; indexing was performed by Powder Cell software\textsuperscript{5} (see Figure S5).

\textit{Computational details and results}

DFT total energy calculations have been performed for different Sc$_2$Ru structural models, relaxed at the equilibrium geometry (in P1 space group) using both the plane wave pseudopotential software QUANTUM-ESPRESSO (QE)\textsuperscript{6} and the all-electron, full-potential FHI-aims package\textsuperscript{7,8}. In both cases, the PBE functional for the exchange and correlation energy was applied. Details on $k$-point mesh chosen to sample the Brillouin zone are reported in Table S3.

\textbf{Table S3.} Used $k$-point meshes for elemental Sc, Ru and Sc$_2$Ru intermetallic with different structures.

| Phase | Structure | $k$-point mesh |
|-------|-----------|----------------|
| Sc    | $hP2$-Mg  | 18 18 12       |
| Sc$_2$Ru | $hP45$-Sc$_2$Ru | 6 6 4      |
|       | $cF96$-Ti$_2$Ni | 6 6 6*       |
|       | $\alpha P12$-Co$_2$Si | 12 14 6    |
|       | $t12$-CuAl$_2$ | 10 10 10     |
|       | $t16$-Mo$_2$Si | 18 18 4      |
| Ru    | $hP2$-Mg  | 20 20 14       |

*calculation performed for the primitive unit cell.

The QE calculations were conducted with the recommended projector-augmented wave (PAW)\textsuperscript{9} pseudopotentials, available at the PSLI library\textsuperscript{10}. The semicore $3s$ and $3p$ states for Sc and the $4s$ and $4p$ for Ru were treated as valence electrons. The plane-wave and density cut-off were set to 56 Ry and 540 Ry, respectively. The orbital occupancies at the Fermi level were treated with a Gaussian smearing of 0.01 Ry. In order to make a comparative analysis of our results with those available at the AFLOW repository, the QE obtained energies have been discussed in the main text for consistency since both QE and VASP are DFT codes based on pseudopotentials. The FHI-aims code was also then used to check the reproducibility of the results. For this purpose, predefined default “tight” basis sets for Sc and Ru were selected including scalar-relativistic effect according to the ZORA approximation. A Gaussian smearing of 0.01 eV was set.

The formation enthalpies ($\Delta_fH$) were evaluated using the calculated total-energies per atom ($E$), according to the following formula: $\Delta_fH = E(Sc_2Ru) - \left[ \frac{2}{3}E(Sc) + \frac{1}{3}E(Ru) \right]$.

These values are listed in Table S4 and shown in Figure S6, together with those available at the AFLOW library calculated with VASP code.
It has to be noted that, though the values of $\Delta H$ slightly differ, the energy differences between the already reported structural models obtained by G.L.W. Hart et al.\textsuperscript{11} are very well reproduced with the computational procedures applied in this work.

**Table S4.** Formation enthalpies $\Delta H$ obtained for different structural models on the basis of DFT (PBE) calculations using different codes.

| Structural model | $hP45$ | $cF96$ | $oP12$ | $t12$ | $t16$ |
|------------------|--------|--------|--------|-------|-------|
| Sc$_2$Ru         |        |        |        |       |       |
| Ti$_2$Ni         | -0.400 | -0.427 | -0.450 | -0.485|
| Co$_2$Si         | -0.449 | -0.376 | -0.398 | -0.427 | -0.461|
| Al$_2$Cu         | -0.456 | -0.384 | -0.409 | -0.434 | -0.470|

**Figure S6.** Formation enthalpies $\Delta H$ plot highlighting similar trends obtained employing different codes.

Finally, using the optimized Sc$_2$Ru–$hP45$ structure the total electron density (ED) was calculated on an equidistant grid of about 0.05 Bohr with the FPLO software\textsuperscript{13}, using an implemented module\textsuperscript{14}. For this calculation, the Brillouin zone was sampled with a 10 $\times$ 10 $\times$ 10 $k$-point mesh employing again the PBE exchange and correlation potential. The atomic basins and their average electronic populations were calculated by means of the DGrid software\textsuperscript{15} on the basis of the Bader’s Quantum Theory of Atoms In Molecules (QTAIM)\textsuperscript{16}. To get the effective charges ($Q^\text{eff}$), atomic populations were subtracted from the atomic numbers. QTAIM basins were visualized thanks to specific plugins for ParaView\textsuperscript{17}.
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