Supplementary material:

High-temperature structural study of decagonal Al-Cu-Rh

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1. Thermal expansion of the lattice constants

**Figure 1** Temperature dependence of the lattice constants. The points marked in red indicate the values for the ~12 Å superstructure annealed at 773 K, quenched and measured at RT.
2. $|F_{T_1}|$ vs. $|F_{T_2}|$ plots for different combinations of $T_1$ and $T_2$

**Figure 2** $|F_{HT}|$ vs. $|F_{293}|$ plots. The red line at 45° angle should serve as guide for the eyes. All data sets were scaled to the calculated (00000) reflection. The points on HT-RT plots are located (mostly) below the red line because of the strong influence of the ADPs on the HT data sets.
Figure 3 |F_HT_1| vs. |F_HT_2| plots. The red line at 45° angle should serve as guide for the eyes. All data sets were scaled to the calculated (00000) reflection.
3. $F_{\text{obs}}$ electron density maps

**Figure 4** 100 x 100 Å$^2$ $F_{\text{obs}}$ electron density map projected along the tenfold axis for the structure at 293 K. The RPT is outlined in grey, PPT in orange and ~33Å "Hiraga cluster" in black. Cluster-flipping is also shown. The clusters outlined in red are located at the “right” positions and the clusters outlined in blue in the “flipped” positions in the typical hexagonal arrangements of RPT tiles. The violet dashed lines indicate the flipped arrangements of tiles, the regions shaded in green show the overlapping region of the clusters in the “right” and in the "flipped" positions. Dashed black lines inside the green-shaded areas show a local mirror-like symmetry in the overlapping regions.
Figure 5 100 x 100 Å$^2$ $F_{\text{obs}}$ electron density map projected along the tenfold axis for the structure at 1013 K.
Figure 6  100 x 100 Å² $F_{\text{obs}}$ electron density map projected along the tenfold axis for the structure at 1083 K.
**Figure 7** 100 x 100 Å$^2$ $F_{\text{obs}}$ electron density map projected along the tenfold axis for the structure at 1153 K.
Figure 8  100 x 100 Å² $F_{\text{obs}}$ electron density map projected along the tenfold axis for the structure at 1223 K.