

## Supporting Information

### **Structural Complexity Meets Transport and Magnetic Anisotropy in Single Crystalline $Ln_{30}Ru_4Sn_{31}$ ( $Ln = Gd-Dy$ )**

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### **Atomic Disorder Refinement**

An electron density peak (Q-peak) was found at  $\sim 2.3$  Å from Gd11, which corresponded to a partially occupied (24(1) %) Ru2' atom; however, the interatomic distance was too close to be considered realistic. Positive and negative Q-peaks were found adjacent to Gd11, suggesting positional disorder. The Gd11 site was found to split between Gd11 (74(2) %) and Gd11' (26(2) %). The Sn12 site was refined to have a negative Q-peak in close proximity to the site, suggesting partial occupancy (87(1) %) or atomic mixing with a smaller atom (Ru). Site mixing of Ru was chosen for the final refinement due to statistical occupancy similarities (described below) and elemental analysis results. Additionally, the Sn12 (74(3) %) and Ru12' (26(3) %) mixed site was found to be positionally disordered when atomic positions were allowed to refine freely. The investigation of positive and negative Q-peaks near Sn11, similar to Gd11, also led to site splitting of Sn11 (75(10) %) and Sn11' (25(10) %). The trend of positional disorder falls

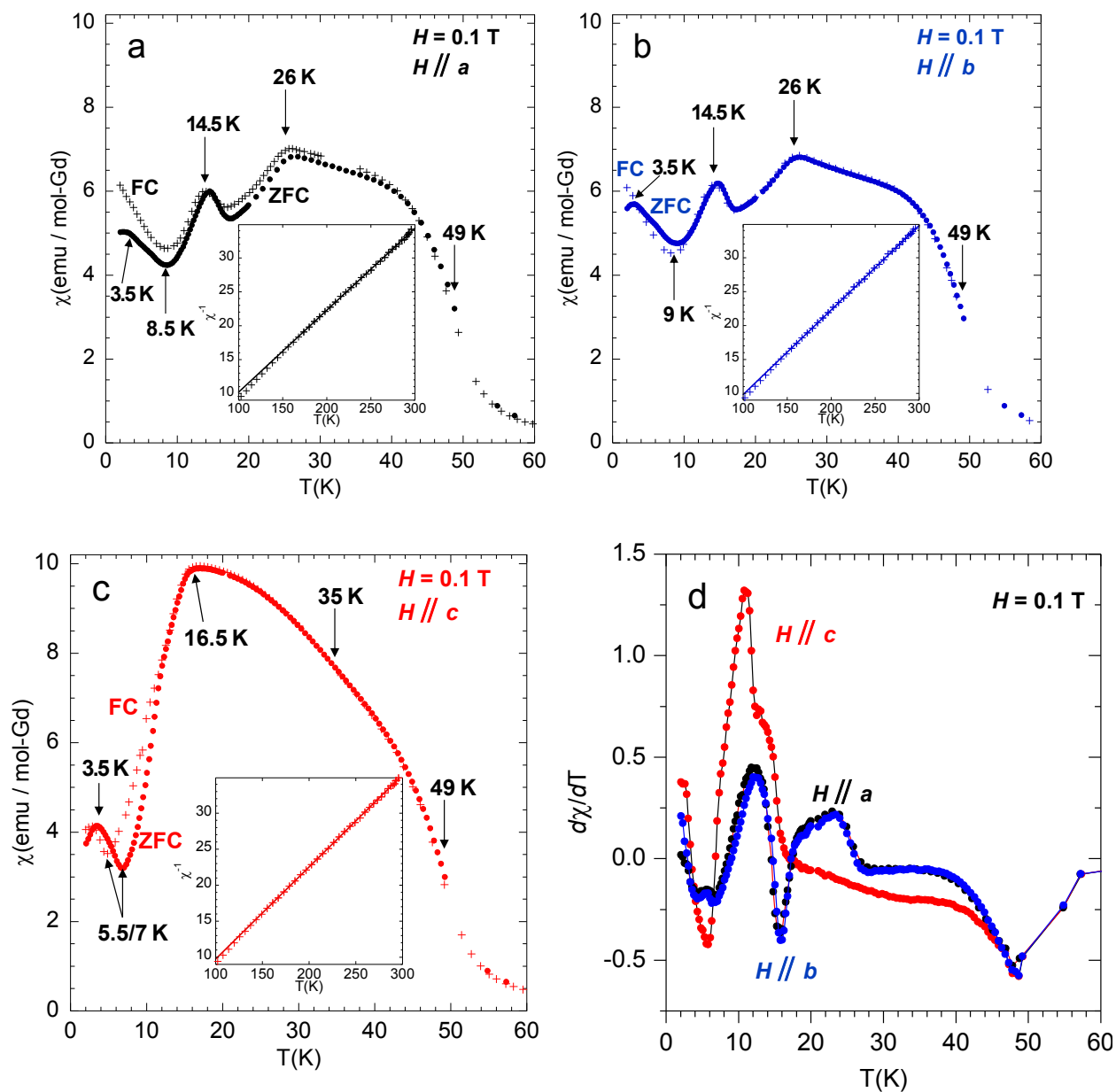
into two groups: **(1)** Gd11 (74(2) %), Sn11 (75(10) %), and Sn12 (74(3) %) and **(2)** Gd11' (26(2) %), Ru12' (26(3) %), Sn11' (25(10) %), and Ru2' (24(1) %). Figure 1a shows the modeled atomic disorder. The Gd–Ru2' interatomic distances were 2.256(5) Å and 2.607(7) Å for Gd11 and Gd11', respectively. Since the occupation difference between Ru2' and Gd11' were statistically insignificant and the short Gd11–Ru2' interatomic distance was chemically unreasonable, the appearance of Gd11' and Ru2' were assumed to occur together, and the occupancies of the two atomic positions were linked. Furthermore, the interatomic distances of the similarly occupied Ru12'–Sn11' (2.76(4) Å), Ru2'–Sn11' (2.72(3) Å), and Sn11–Sn12 (2.983(9) Å) fall within the range of Ru–Sn (2.57–2.78 Å) and Sn–Sn (2.89–3.14 Å) interatomic distances found in other *A*–Ru–Sn intermetallic compounds.<sup>26-28</sup> The interatomic distances of the non-similarly occupied site Ru12'–Sn11 (2.84(2) Å) falls outside the aforementioned range. Because of the more chemically reasonable interatomic distances and the statistically insignificant deviations in occupancy, the site occupancy factors of all the similarly occupied positions were linked for final refinements.

### **Supporting Details of the Polyhedral Sn1, Sn7, Sn8, and Sn9 Structural Units**

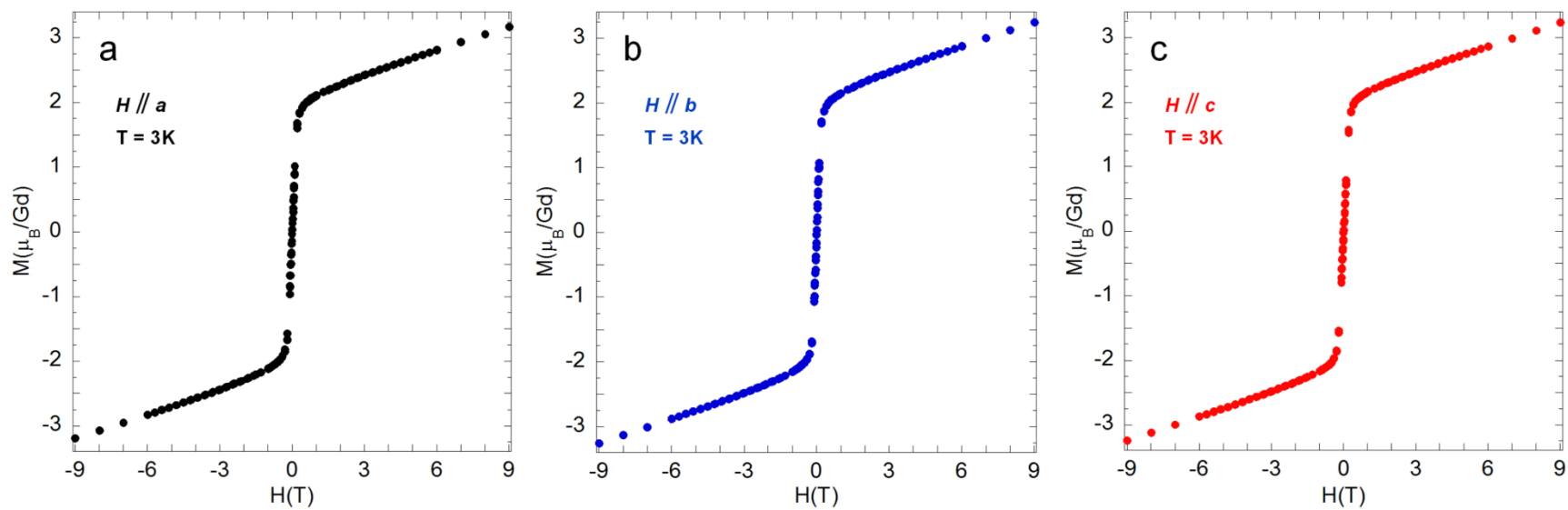
The alternating units described in the main text can be viewed as “zig” and “zag” units, which extend infinitely in the *a-c* plane. A shorthand  $Y(X_1, X_2, \dots)$ , where *Y* is the atom type and  $X_x$  is the atomic site, is used for descriptions of shared polyhedral vertices. The “zig” set is composed of confacial Sn7 polyhedra which are triangular face sharing ( $\times 8$ ) by Gd(5,6,7) atoms with four Sn9 polyhedra in a square planar configuration along the confacial equatorial plane of the two Sn7 polyhedra. These “zig” units are connected along the *c*-direction with edge-sharing Sn9 polyhedra ( $\times 4$ ) by Gd(3,11) atoms from two adjacent “zig” units which form gaps shown

in Figure 4f, allowing the Ru–Sn, Sn–Sn framework to penetrate between slabs. The “zag” set is constructed of confacial Sn1 polyhedra which are triangular face sharing ( $\times 4$ ) by Gd(8,8,10) atoms with two sets of axially oriented confacial Sn8 polyhedra. The confacial plane of the Sn1 polyhedral units connects “zag” units in the *c*-direction. The sheets are bridged by the “zag” Sn1 and Sn8 polyhedra. Confacial Sn1 polyhedra link the sheets with triangular face sharing ( $\times 4$ ) by Gd(3,8,10) atom with four Sn9 polyhedra and corner sharing ( $\times 4$ ) by Gd8 atoms with four Sn7 polyhedron. Sn8 confacial polyhedra bridge the sheets with triangular face sharing ( $\times 4$ ) by Gd(6,8,10) atoms with four Sn9 polyhedra and triangular face sharing ( $\times 2$ ) by Gd(6,8,8) atoms with two sets of Sn7 confacial polyhedra.

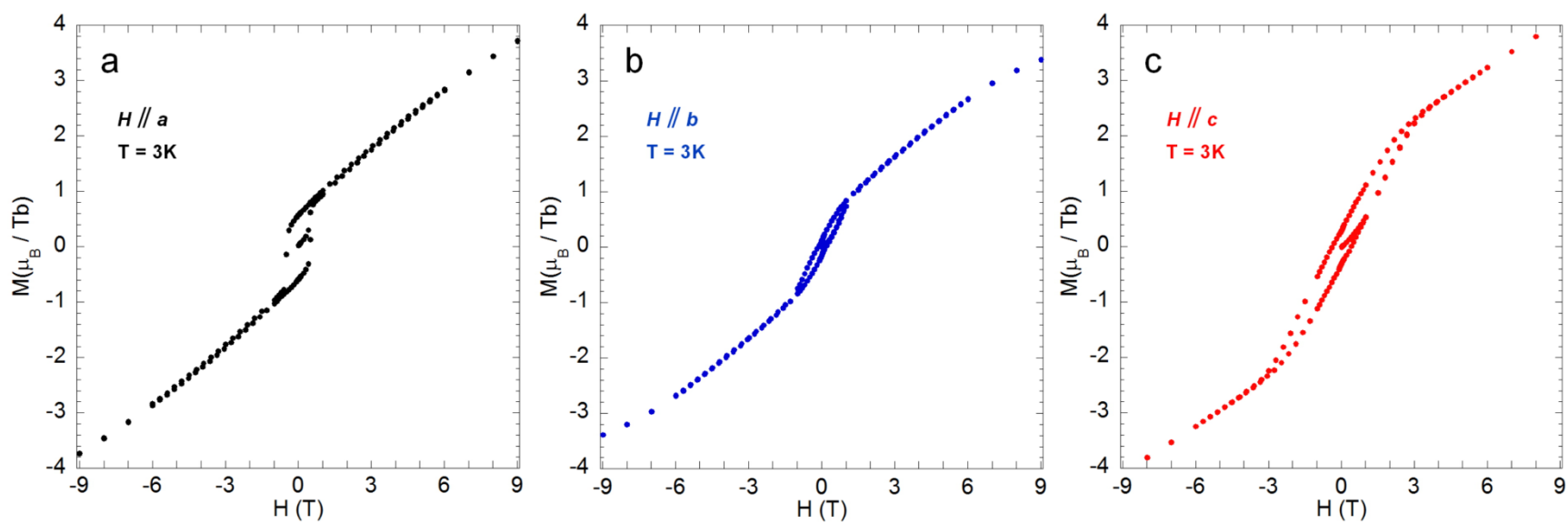
## Supporting Figures



**Figure S1.** Temperature-dependent ZFC and FC magnetic susceptibility of  $\text{Gd}_{30}\text{Ru}_{4.92}\text{Sn}_{30.54}$  from 2–70 K in an applied field of 0.1 T with (a)  $H // a$ , (b)  $H // b$ , and (c)  $H // c$ . Arrows show the magnetic transition temperatures, and insets show inverse susceptibility plots with extrapolated linear fits from the modified Curie-Weiss fit regions. (d) shows the temperature-dependent derivative of the ZFC magnetic susceptibility with  $H // a$ ,  $b$ , and  $c$ .



**Figure S2.** Field-dependent magnetization of  $\text{Gd}_{30}\text{Ru}_{4.92}\text{Sn}_{30.54}$  at 3 K in applied fields up to 9 T with (a)  $H // a$ , (b)  $H // b$ , and (c)  $H // c$  shown in black, blue, and red, respectively.



**Figure S3.** Field-dependent magnetization of  $\text{Tb}_{30}\text{Ru}_6\text{Sn}_{29.5}$  at 3 K in applied fields up to 9 T with (a)  $H // a$ , (b)  $H // b$ , and (c)  $H // c$  shown in black, blue, and red, respectively.

## Supporting Tables

**Table S1a.** Positions, occupancies, and atomic displacement parameters for Tb<sub>30</sub>Ru<sub>6</sub>Sn<sub>29.5</sub>

| Atom  | Site | <i>x</i>   | <i>y</i>     | <i>z</i>   | Occ.     | $U_{\text{eq}} (\text{\AA}^2)^a$ |
|-------|------|------------|--------------|------------|----------|----------------------------------|
| Tb1   | 4g   | 0.13793(4) | 0.658250(17) | 0          | 1        | 0.01038(8)                       |
| Tb2   | 4g   | 0.59003(3) | 0.898000(17) | 0          | 1        | 0.00943(8)                       |
| Tb3   | 4g   | 0.26482(3) | 0.969769(17) | 0          | 1        | 0.00933(8)                       |
| Tb4   | 4g   | 0.78423(4) | 0.801697(17) | 0          | 1        | 0.01106(9)                       |
| Tb5   | 4e   | 0          | 0            | 0.26695(3) | 1        | 0.00881(8)                       |
| Tb6   | 4g   | 0.32487(4) | 0.418402(18) | 0          | 1        | 0.01350(9)                       |
| Tb7   | 8h   | 0.44070(2) | 0.652902(12) | 0.81881(3) | 1        | 0.00996(6)                       |
| Tb8   | 8h   | 0.82086(2) | 0.473606(12) | 0.17554(2) | 1        | 0.00891(6)                       |
| Tb9   | 8h   | 0.73165(3) | 0.720418(12) | 0.26150(3) | 1        | 0.01129(6)                       |
| Tb10  | 8h   | 0.42996(2) | 0.882974(12) | 0.26191(3) | 1        | 0.01087(6)                       |
| Tb11  | 4g   | 0.93699(9) | 0.14084(5)   | 0          | 0.765(3) | 0.01297(19)                      |
| Tb11' | 4g   | 0.9344(4)  | 0.12428(15)  | 0          | 0.235(3) | 0.01297(19)                      |
| Ru1   | 8h   | 0.51232(4) | 0.78732(2)   | 0.12516(4) | 1        | 0.00900(9)                       |
| Ru2'  | 4g   | 0.1275(3)  | 0.77376(12)  | 0          | 0.235(3) | 0.0124(9)                        |
| Sn1   | 4f   | 0          | 0.5          | 0.36319(5) | 1        | 0.00890(11)                      |
| Sn2   | 2a   | 0          | 0            | 0          | 1        | 0.01467(18)                      |
| Sn3   | 4g   | 0.35208(5) | 0.84930(2)   | 0          | 1        | 0.01144(12)                      |
| Sn4   | 8h   | 0.83766(3) | 0.921609(17) | 0.12585(3) | 1        | 0.00909(8)                       |
| Sn5   | 4g   | 0.34328(5) | 0.73545(2)   | 0          | 1        | 0.01103(12)                      |
| Sn6   | 4g   | 0.61468(6) | 0.70589(2)   | 0          | 1        | 0.01251(12)                      |
| Sn7   | 4g   | 0.62056(5) | 0.44425(2)   | 0          | 1        | 0.01033(11)                      |
| Sn8   | 4g   | 0.95719(5) | 0.55853(3)   | 0          | 1        | 0.01203(12)                      |
| Sn9   | 8h   | 0.67441(4) | 0.591628(17) | 0.26484(4) | 1        | 0.01041(8)                       |
| Sn10  | 8h   | 0.67872(3) | 0.844945(16) | 0.23586(3) | 1        | 0.00818(8)                       |
| Sn11  | 8h   | 0.9817(3)  | 0.74805(12)  | 0.8477(3)  | 0.765(3) | 0.0100(3)                        |
| Sn11' | 8h   | 0.9736(11) | 0.7415(5)    | 0.8394(12) | 0.235(3) | 0.0100(3)                        |
| Sn12' | 4g   | 0.85907(6) | 0.67606(3)   | 0          | 0.235(3) | 0.01065(13)                      |
| Ru12  | 4g   | 0.85907(6) | 0.67606(3)   | 0          | 0.765(3) | 0.01065(13)                      |

<sup>a</sup>  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

' Positional and/or occupational disorder of Tb11, Sn11, and Ru12 with Tb11', Sn11', and Sn12', respectively. Ru2' occurs at the same frequency as the disordered atoms.

**Table S1b.** Positions, occupancies, and atomic displacement parameters for Dy<sub>30</sub>Ru<sub>4.57</sub>Sn<sub>30.72</sub>

| Atom  | Site | <i>x</i>    | <i>y</i>     | <i>z</i>   | Occ.     | $U_{\text{eq}} (\text{\AA}^2)^a$ |
|-------|------|-------------|--------------|------------|----------|----------------------------------|
| Dy1   | 4g   | 0.13966(5)  | 0.65820(2)   | 0          | 1        | 0.01032(12)                      |
| Dy2   | 4g   | 0.58950(5)  | 0.89952(2)   | 0          | 1        | 0.00984(11)                      |
| Dy3   | 4g   | 0.26454(5)  | 0.96973(2)   | 0          | 1        | 0.00956(11)                      |
| Dy4   | 4g   | 0.78056(5)  | 0.80377(2)   | 0          | 1        | 0.01091(12)                      |
| Dy5   | 4e   | 0           | 0            | 0.26642(5) | 1        | 0.00920(11)                      |
| Dy6   | 4g   | 0.32926(5)  | 0.41950(2)   | 0          | 1        | 0.01168(12)                      |
| Dy7   | 8h   | 0.43876(3)  | 0.652200(16) | 0.81957(3) | 1        | 0.01029(9)                       |
| Dy8   | 8h   | 0.82077(3)  | 0.474047(16) | 0.17489(3) | 1        | 0.00974(8)                       |
| Dy9   | 8h   | 0.73531(3)  | 0.720583(16) | 0.25956(3) | 1        | 0.01150(9)                       |
| Dy10  | 8h   | 0.43038(3)  | 0.884754(16) | 0.25933(3) | 1        | 0.00941(8)                       |
| Dy11  | 4g   | 0.93590(10) | 0.14039(6)   | 0          | 0.858(4) | 0.0123(2)                        |
| Dy11' | 4g   | 0.9337(8)   | 0.1243(3)    | 0          | 0.142(4) | 0.0123(2)                        |
| Ru1   | 8h   | 0.50942(6)  | 0.78866(3)   | 0.12626(6) | 1        | 0.00937(13)                      |
| Ru2'  | 4g   | 0.1327(6)   | 0.7747(3)    | 0          | 0.142(4) | 0.0089(19)                       |
| Sn1   | 4f   | 0           | 0.5          | 0.36117(7) | 1        | 0.00929(15)                      |
| Sn2   | 2a   | 0           | 0            | 0          | 1        | 0.0122(2)                        |
| Sn3   | 4g   | 0.35143(7)  | 0.85057(3)   | 0          | 1        | 0.01095(17)                      |
| Sn4   | 8h   | 0.83729(5)  | 0.92181(2)   | 0.12630(5) | 1        | 0.00947(11)                      |
| Sn5   | 4g   | 0.34128(7)  | 0.73608(3)   | 0          | 1        | 0.01109(17)                      |
| Sn6   | 4g   | 0.60542(7)  | 0.70708(3)   | 0          | 1        | 0.00976(16)                      |
| Sn7   | 4g   | 0.62087(7)  | 0.44478(3)   | 0          | 1        | 0.01059(16)                      |
| Sn8   | 4g   | 0.95902(7)  | 0.55662(3)   | 0          | 1        | 0.01022(16)                      |
| Sn9   | 8h   | 0.67345(5)  | 0.59240(2)   | 0.26343(5) | 1        | 0.01059(12)                      |
| Sn10  | 8h   | 0.67730(5)  | 0.84531(2)   | 0.23683(5) | 1        | 0.00861(11)                      |
| Sn11  | 8h   | 0.9851(4)   | 0.74859(18)  | 0.8467(4)  | 0.858(4) | 0.0100(4)                        |
| Sn11' | 8h   | 0.982(3)    | 0.7536(12)   | 0.836(2)   | 0.142(4) | 0.0100(4)                        |
| Sn12  | 4g   | 0.8532(6)   | 0.6762(3)    | 0          | 0.858(4) | 0.0103(6)                        |
| Ru12' | 4g   | 0.864(5)    | 0.681(2)     | 0          | 0.142(4) | 0.0103(6)                        |

<sup>a</sup>  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>†</sup> Positional and/or occupational disorder of Dy11, Sn11, and Sn12 with Dy11', Sn11', and Ru12', respectively. Ru2' occurs at the same frequency as the disordered atoms.