**Two-Dimensional Frank-Kasper *Z* Phase with One Unit-Cell Thickness**

**Supplementary Information**

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**1. Materials and Methods**

**1.1 Experimental procedure**

The alloy with nominal composition of Mg-4.0wt%Sm-2.0wt%Zn (Mg-0.68at.%Sm-0.78at.%Zn) was prepared by melting the pure Mg (99.9 wt%), pure Zn (99.9 wt%), and Mg-25Sm (wt%) master alloy in the induction furnace with protection of the argon atmosphere. The molten alloy was stirred and kept at 760 ºC for 5 minutes and poured into a steel mold preheated to 300 ºC. The chemical composition of as-cast ingot was measured by OPTIMA 4300 DV composition analyzer, and the actual composition was determined to be Mg-4.12wt% Sm-2.07wt%Zn. The as-cast samples were solution treated at 520 ºC for 12h, followed by water quenching and ageing in oil bath at 200 ºC for different times, and finally continued isothermally aged at 250 ºC for 2 h.

The TEM specimens with a diameter of 3 mm were prepared by twin jet electro-polishing at - 40 ºC in mixture solution of 5.3 g lithium chloride, 11.2 g magnesium perchlorate, 500 ml methanol and 100 ml 2-butoxy ethanol, and subsequently ion milling with low energy electron beam. Finally, [Gatan SOLARUS (950) Plasma Cleaning System](https://www.baidu.com/link?url=Ddut1mcKh7wTOcxcJpYBffc5ncp2yrMzyOkePlH0itTgXcaq1ICoWpbF9FaSfrKTsHqUDjqwyUaOyiJzaPmsCK&wd=&eqid=f017f6150001a3ff0000000359c0ef22) was used to clean up the sample surfaces. TEM and STEM observation was carried out by using the JEM-ARM200F at an accelerating voltage of 200 kV, equipped with probe Cs corrector and cold field emission gun. The probe convergence is 25 mrad which yields a probe size of less than 0.1 nm, and the camera length was set to 8 cm which yields a collection semi-angle of 48-327 mrad.

Crystal structures were reconstructed by the *CrystalMaker.CrystalMaker.v2.2.4* software, and then the electron diffraction patterns of the precipitated phase detected from the [0001], , and directions were simulated by using *CrystalMaker.SingleCrystal.v2.0.1*.

**1.2 Computational methods**

The first-principles calculations were conducted using the Vienna *ab-initio* simulation package (VASP)[1] with projector augmented-wave (PAW)[2, 3] pseudopotentials. The exchange-correlation potential was described by the generalized gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE)[4]. A high plane-wave cutoff energy of 500eV and dense *k*-point sampling based Gamma-centered Monkhorst-pack scheme are employed to guarantee high numerical accuracy. The geometry optimization process were performed using a conjugate gradient algorithm until the final force on each atom was less than 0.01 eV/Å.

The formation energy, *Ef*, can approximately characterize the stability of compounds in thermodynamics[5]. And the formation energies in present calculations, , were calculated as following equation:

Here,represent the total energy of the model, the energies of Mg, Sm and Zn unit cell, respectively. The charge distribution and Electron Localized Function (ELF) models were displayed by using the VESTA software.

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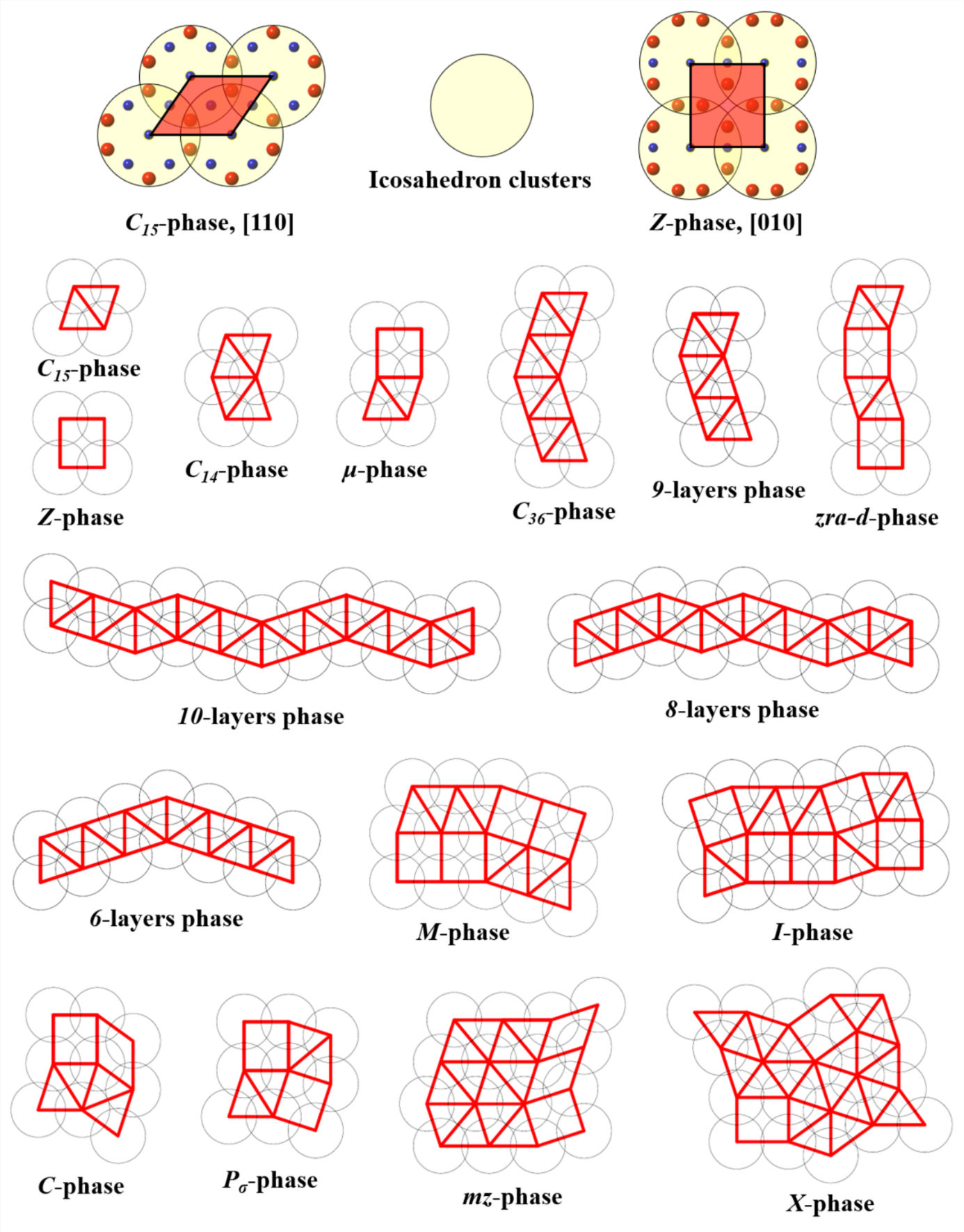
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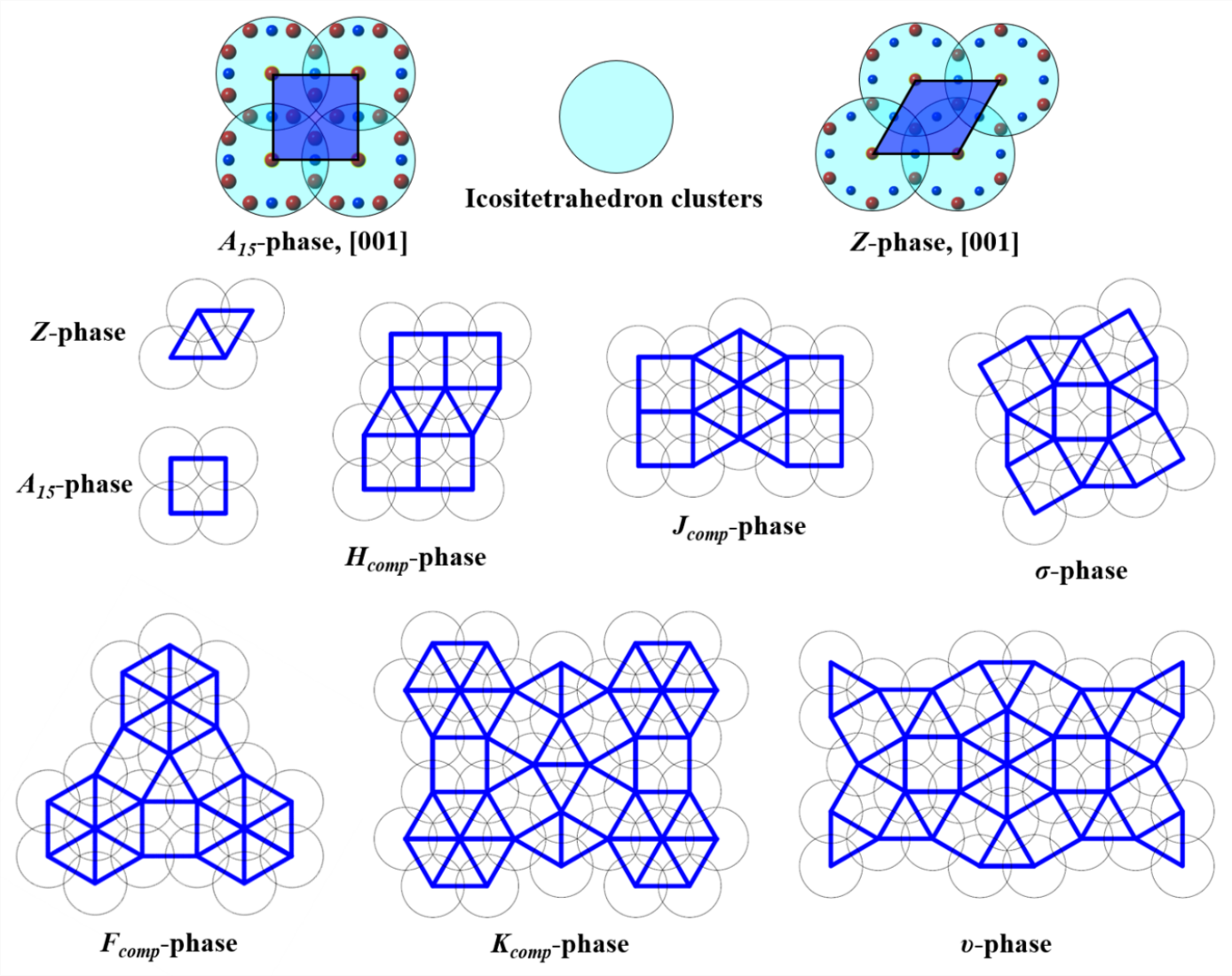
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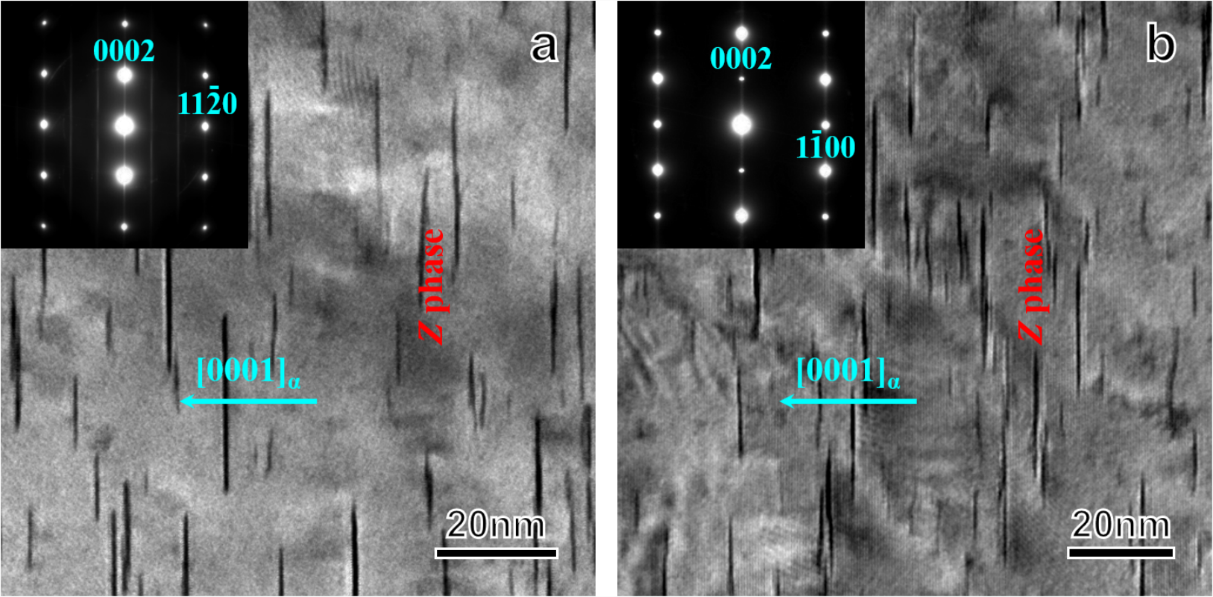
**2. Supplementary Figures**



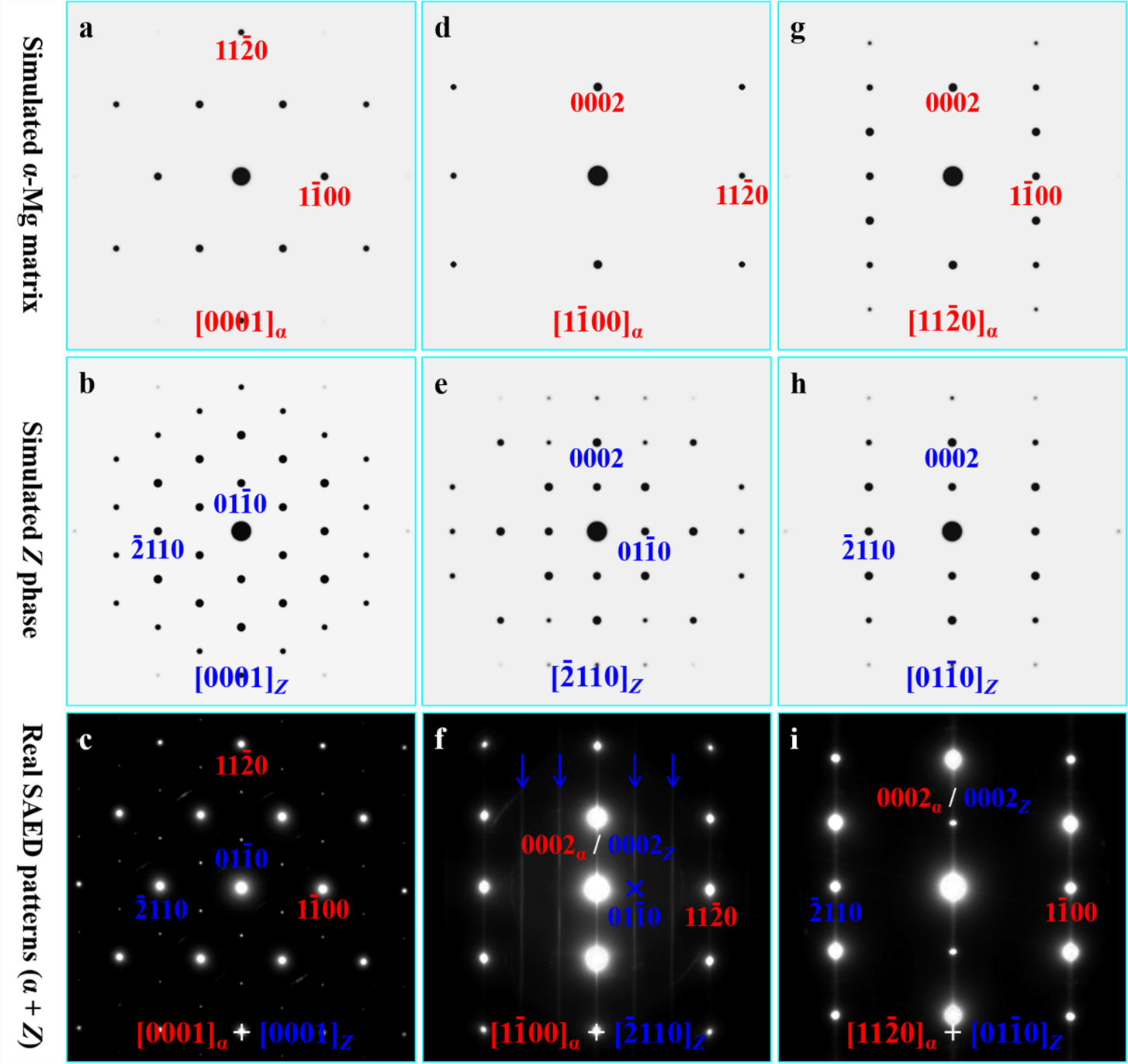
**Figure S1.** Schematic diagrams of the *pentagonal* Frank-Kasper phases, which assembled by the *C15* and *Z* plane tiling patterns. And it can be seen that these Frank-Kasper phases are arranged along the pseudo ten-fold axis by the icosahedron columns.



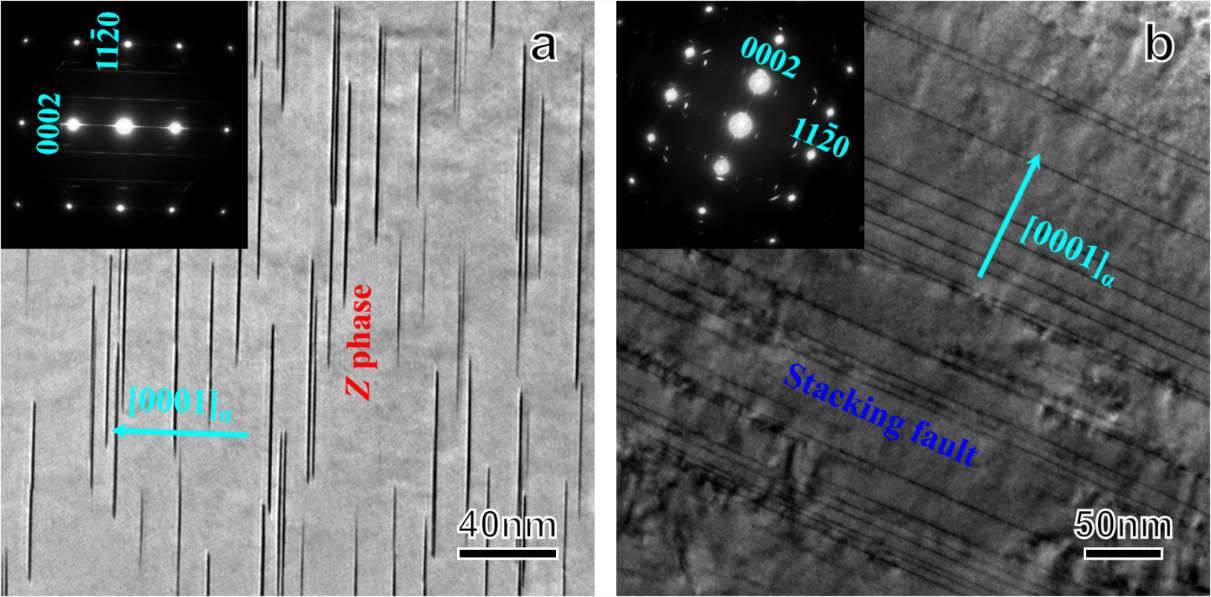
**Figure S2.** Schematic diagrams of the *hexagonal* Frank-Kasper phases, which assembled by the *A15* and *Z* plane tiling patterns. And it can be seen that these Frank-Kasper phases are arranged along the pseudo twelve-fold axis by the icositetrahedron columns.



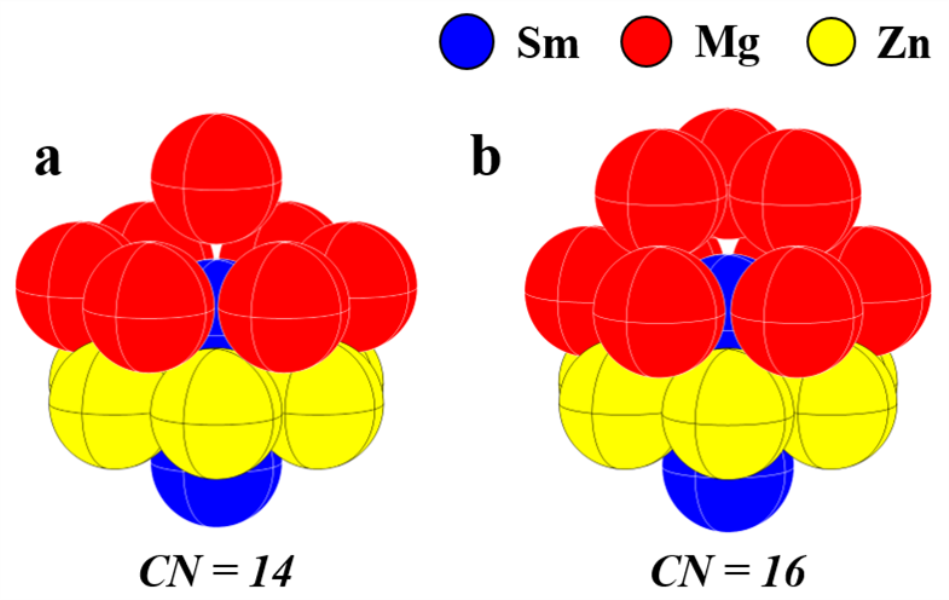
**Figure S3.** Bright-field images showing the 2D Frank-Kasper *Z* phase precipitated in the Mg-4Sm-2Zn alloy after aged at 200 ºC for 48 h. The electron beam is parallel to the *α* (a) and *α* (b). The insets are the corresponding selected-area electron diffraction (SAED) patterns.



**Figure S4.** Electron diffraction results. (a, d, and g)Simulated electron diffraction patterns of the *α*-Mg matrix from [0001]*α* (a), *α* (d), and *α* (g). (b, e, and h)Simulated electron diffraction prtterns of the 2D Frank-Kasper*Z*-Mg*2*Sm*2*Zn*3* phase from [0001]*z* (b), *z* (e), and *z* (h). (c, f, and i) Select-area electron diffraction (SAED) patterns of the 2D Frank-Kasper *Z*-Mg*2*Sm*2*Zn*3* precipitate in the Mg-Sm-Zn alloy from [0001]*α*+*z* (c), *α* + *z* (f), and *α* + *z* (i). It can be found that the simulation results are consistent with the experimental results, in which without considering the {0001}*z* basal planes diffraction. Since 2D Frank-Kasper *Z*-Mg*2*Sm*2*Zn*3* precipitate only has a single unit-cell height in the [0001]*z* direction, and it has also no periodicity along the [0001]*z* direction, the diffraction streaks parallel to the [0001]*z* direction are observed in the actual electron diffraction patterns.



**Figure S5.** (a)Bright-field image of the Mg-4Sm-2Zn alloy after aged at 200 ºC for 100 h. (b) Bright-field image of the Mg-4Sm-2Zn alloy subjected to continuous isothermal aging at 250 ºC for 2 h. The electron beam is parallel to the *α* direction. The insets are the corresponding SAED patterns.



**Figure S6.** Atomic cluster models: (a) *CN* = 14, icositetrahedron; (b) *CN* = 16, irregular polyhedron.

**3. Supplementary Tables**

**Table S1.** Crystallographic parameters of the Feank-Kasper phases [1-24].

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Phase** | **Representative alloy** | **Space group** | **Lattice parameters (*Å*)** | | | | **Atomic Number** | ***CN* (*%*)** | | | | | ***Ref.*** |
| ***a*** | ***b*** | ***c*** | ***β* (°)** | **16** | **15** | **14** | **12** | ***A. V.*** |
| **1** | **A15** | **Cr3Si** | ***Pmn*** | **4.560** | **4.560** | **4.560** |  | **8** | **0** | **0** | **75.0** | **25.0** | **13.50** | **[1]** |
| 2 | σ | Cr46Fe54 | *P42/mnm* | 8.797 | 8.797 | 4.559 |  | 30 | 0 | 13.3 | 53.4 | 33.3 | 13.47 | [2] |
| 3 | H | Complex | *Cmmm* | 4.500 | 17.500 | 4.500 |  | 30 | 0 | 13.3 | 53.4 | 33.3 | 13.47 | [3, 4] |
| 4 | K | Complex | *Pmmm* | 12.500 | 17.100 | 4.500 |  | 82 | 0 | 14.6 | 51.2 | 34.2 | 13.46 | [3, 4] |
| 5 | F | Complex | *P6/mmm* | 12.500 | 12.500 | 4.500 |  | 52 | 0 | 15.4 | 50.0 | 34.6 | 13.46 | [3, 4] |
| 6 | J | Complex | *Pmmm* | 4.500 | 12.500 | 4.500 |  | 22 | 0 | 18.2 | 45.5 | 36.3 | 13.46 | [3, 4] |
| 7 | υ | Mn81.5Si18.5 | *Immm* | 16.992 | 28.634 | 4.656 |  | 186 | 6.5 | 10.5 | 43.0 | 40.0 | 13.43 | [5] |
| **8** | **Z** | **Zr4Al3** | ***P6/mmm*** | **5.433** | **5.433** | **5.390** |  | **7** | **0** | **28.6** | **28.6** | **42.8** | **13.43** | **[6]** |
| 9 | P | Mo42Cr18Ni40 | *Pbnm* | 9.07 | 17.01 | 4.74 |  | 56 | 7.1 | 14.3 | 35.7 | 42.9 | 13.43 | [7] |
| 10 | δ | MoNi | *P212121* | 9.108 | 9.108 | 8.852 |  | 56 | 7.1 | 14.3 | 35.7 | 42.9 | 13.43 | [8] |
| 11 | K | Mn77Fe4Si19 | *C2* | 13.362 | 11.645 | 8.734 | 90.5 | 220 | 12.7 | 7.3 | 34.5 | 45.5 | 13.41 | [9] |
| 12 | R | Mo31Cr51Co18 | *R* | 10.903 | 10.903 | 19.342 |  | 159 | 15.1 | 11.3 | 22.6 | 51.0 | 13.40 | [10] |
| 13 | μ | Mo6Co7 | *Rm* | 4.762 | 4.762 | 25.615 |  | 39 | 15.4 | 15.4 | 15.4 | 53.8 | 13.39 | [11] |
| 14 | zra-d | K7Cs6 | *P63/mmc* | 9.078 | 9.078 | 32.950 |  | 26 | 15.4 | 15.4 | 15.4 | 53.8 | 13.39 | [12] |
| 15 | Pσ | W6(Fe, Si)7 | *Pbam* | 9.283 | 7.817 | 4.755 |  | 26 | 15.4 | 15.4 | 15.4 | 53.8 | 13.39 | [13] |
| 16 | M | Nb48Ni39Al13 | *Pnma* | 9.303 | 4.933 | 16.266 |  | 52 | 15.4 | 15.4 | 15.4 | 53.8 | 13.39 | [14] |
| 17 | I | V41Ni36Si23 | Cc | 13.462 | 23.381 | 8.940 | 100.3 | 228 | 21.1 | 10.5 | 10.5 | 57.9 | 13.37 | [15] |
| 18 | C | V2(Co, Si)3 | *C2/m* | 17.170 | 4.660 | 17.62 | 155 | 50 | 24.0 | 8.0 | 8.0 | 60.0 | 13.36 | [16] |
| 19 | T | Mg32(Zn, Al)49 | *Im* | 14.160 | 14.160 | 14.160 |  | 162 | 24.7 | 7.4 | 7.4 | 60.5 | 13.36 | [17] |
| 20 | X | Mn45Co40Si15 | *Pnnm* | 15.500 | 12.470 | 4.760 |  | 74 | 27.0 | 5.4 | 5.4 | 62.2 | 13.35 | [18] |
| 21 | mz | Mg4Zn7 | *C2/m* | 25.960 | 5.240 | 14.280 | 102.5 | 110 | 29.1 | 3.6 | 3.6 | 63.7 | 13.34 | [19] |
| 22 | 6-layers | MgCuNi | *P63/mmc* | 4.917 | 4.917 | 24.040 |  | 36 | 33.3 | 0 | 0 | 66.7 | 13.33 | [20] |
| 23 | 8-layers | MgZn2+0.03MgAg2 | *P63/mmc* | 5.210 | 5.210 | 34.400 |  | 48 | 33.3 | 0 | 0 | 66.7 | 13.33 | [21] |
| 24 | 9-layers | MgZn2+0.07MgAg2 | *Rm* | 5.210 | 5.210 | 38.700 |  | 54 | 33.3 | 0 | 0 | 66.7 | 13.33 | [21] |
| 25 | 10-layers | MgZn2+0.1MgAg2 | *P63/mmc* | 5.220 | 5.220 | 43.000 |  | 60 | 33.3 | 0 | 0 | 66.7 | 13.33 | [21] |
| 26 | C14 | MgZn2 | *P63/mmc* | 5.223 | 5.223 | 8.566 |  | 12 | 33.3 | 0 | 0 | 66.7 | 13.33 | [22] |
| 27 | C36 | MgNi2 | *P63/mmc* | 4.824 | 4.824 | 15.826 |  | 24 | 33.3 | 0 | 0 | 66.7 | 13.33 | [23] |
| **28** | **C15** | **MgCu2** | ***Fdm*** | **7.061** | **7.061** | **7.061** |  | **24** | **33.3** | **0** | **0** | **66.7** | **13.33** | **[24]** |

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**Table S2.** Structure parameters of the 2D Frank-Kasper *Z*-Mg*2*Sm*2*Zn*3* phase.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Chemical formula** | **Atom number in cell** | **Space group** | **Lattice parameter** | **Atom site** |
| Mg*2*Sm*2*Zn*3* | 7 | *P6/mmm* | *α* = *β* = 90º, *γ* = 120º;  *a* = 5.66 Å, *c* = 4.79 Å | Mg: 2c (0.3333, 0.6667, 0);  Sm: 2e (0, 0, 0.1238);  Zn: 6i (0.500, 0, 0.500) |

**Table S3.** First-principles computations results for the 2D Frank-Kasper *Z*-Mg*2*Sm*2*Zn*3* phase.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **No.** | **Stacking model** | **Formation**  **energy (*meV*)** | **Lattice parameter (*Å*)** | | |
| ***a*** | ***c*** | ***HSm-Sm*** |
| 0+0 | -A’CA’- | 38.54 | 5.50 | 5.18 | 3.31 |
| 1+2 | B-A’CA’-BA | -117.85 | 5.58 | 4.85 | 3.52 |
| **2+3** | **AB-A’CA’-BAB** | **-88.19** | **5.57** | **4.85** | **3.53** |
| 2+3 | BA-A’CA’-ABA | -18.79 | 5.50 | 5.01 | 3.33 |
| 3+4 | BAB-A’CA’-BABA | -69.52 | 5.56 | 4.86 | 3.53 |
| 4+5 | ABAB-A’CA’-BABAB | -58.09 | 5.55 | 4.88 | 3.52 |
| 5+6 | BABAB-A’CA’-BABABA | -50.52 | 5.55 | 4.87 | 3.53 |
| 6+7 | ABABAB-A’CA’-BABABAB | -44.26 | 5.56 | 4.87 | 3.50 |

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