Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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ANALYSES OF THE INTERFACE REGIONS BASED ON TRADITIONAL “LAYERING AND IN-PLANE ORDERING” FRAMEWORK

Following **Figure S1~S3** are the analytical results based on the framework of “layering and in-plane ordering”. Also included are the results of hyperbolic tangent fitting of two representative order parameters, aq_6 and Frenkel number (FN).

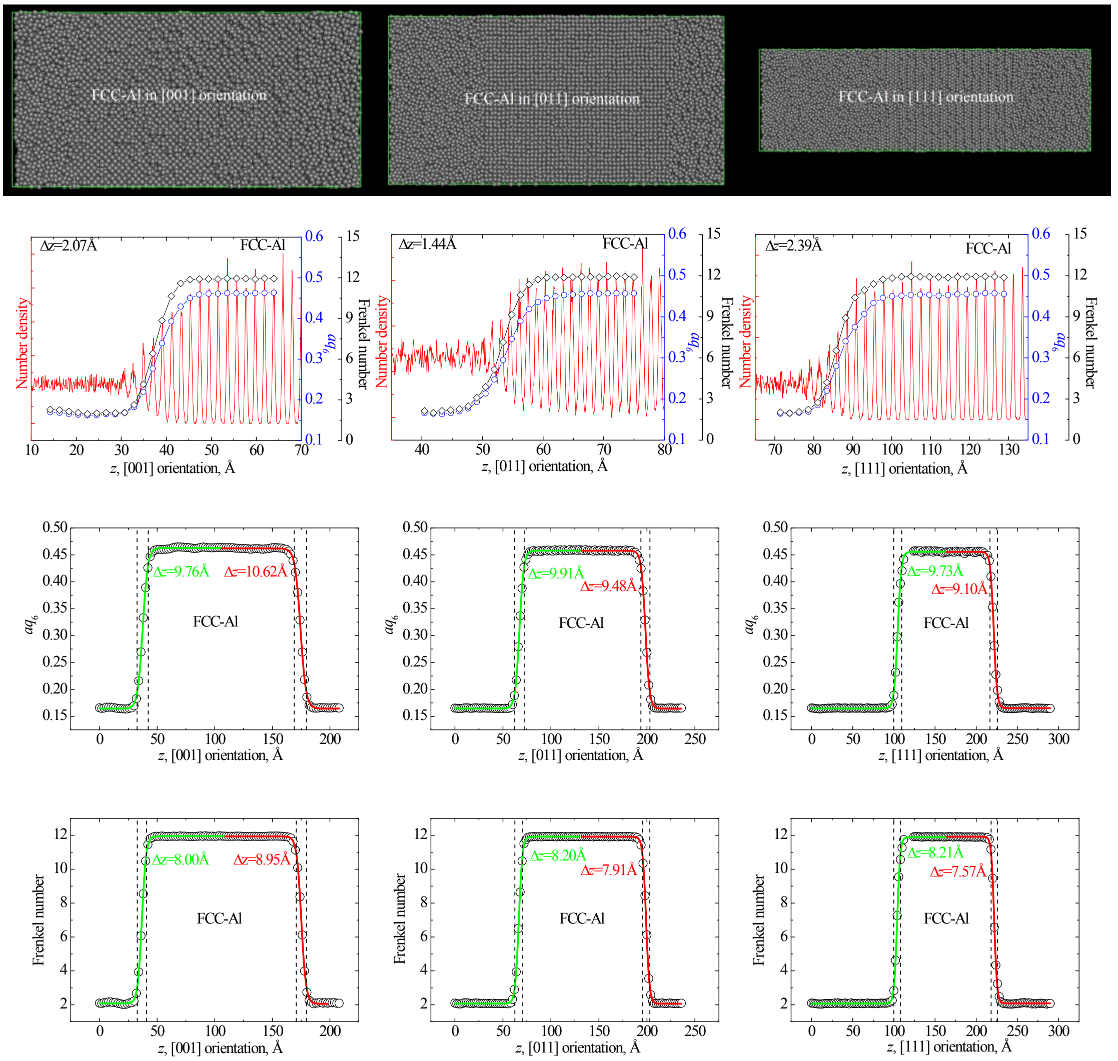


Figure S1. Three representative snapshots, the decaying oscillation of number density, and the slice-wise profiles of aq_6 and FN and their hyperbolic tangent fittings of FCC-Al based on the framework of “layering and in-plane ordering”.

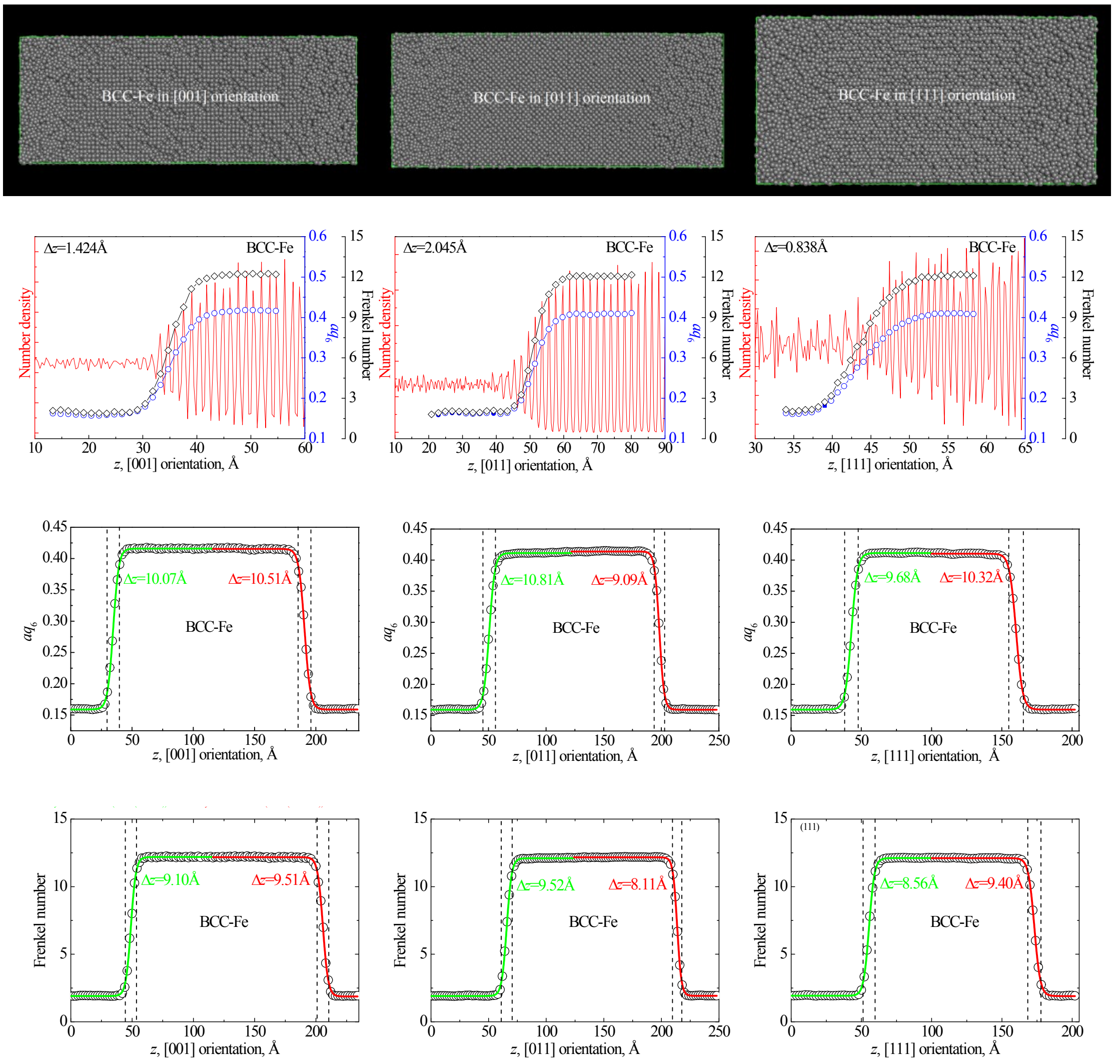


Figure S2. Three representative snapshots, the decaying oscillation of number density, and the slice-wise profiles of aq_6 and FN and their hyperbolic tangent fittings of BCC-Fe based on the framework of "layering and in-plane ordering".

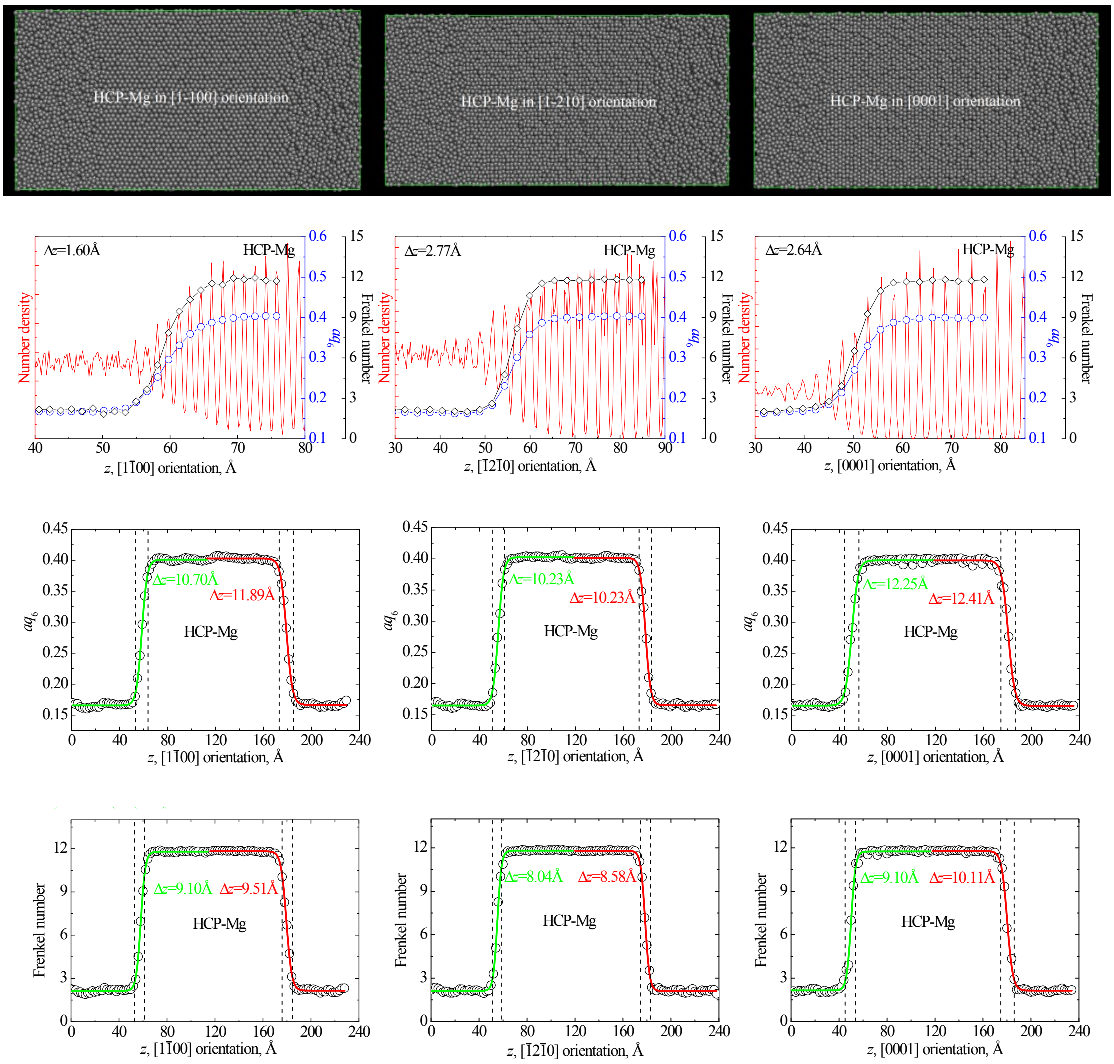
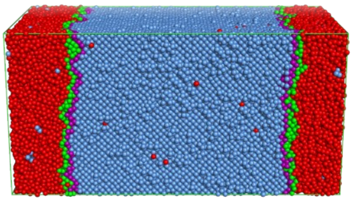
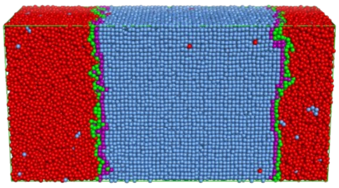


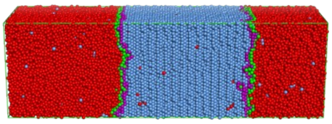
Figure S3. Three representative snapshots, the decaying oscillation of number density, and the slice-wise profiles of aq_6 and FN and their hyperbolic tangent fittings of HCP-Mg based on the framework of "layering and in-plane ordering".

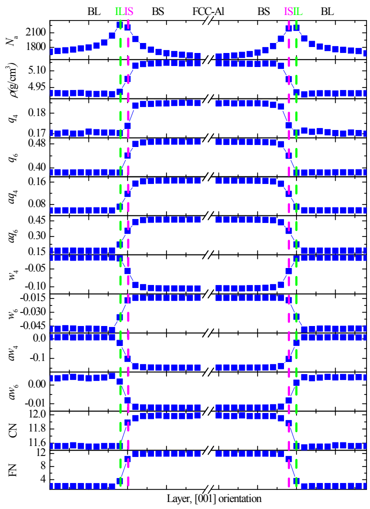
ANALYSES OF INTERFACES BASED ON CBS FRAMEWORK

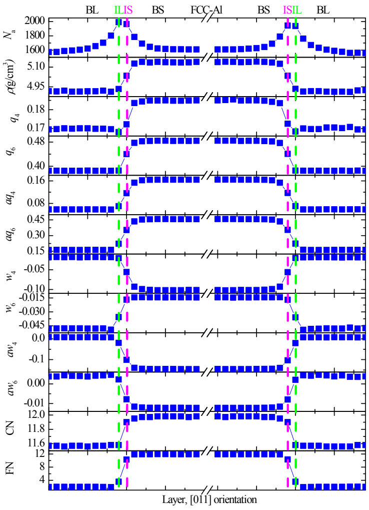
Following **Figure S4~S6** are the analytical results based on the framework of CBS. The properties contain the average atom number N_a, the average density ρ; BOO parameters (i.e. q_4, q_6, w_4, and w_6); ABOO parameters (i.e. aq_4, aq_6, aw_4 and aw_6); coordinate number (CN); and Frenkel number (FN). Also exhibited are the fraction distributions of four atom types.

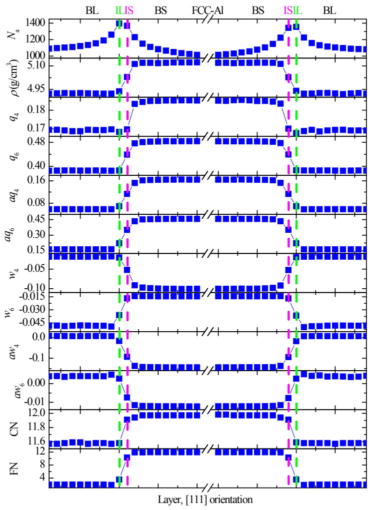












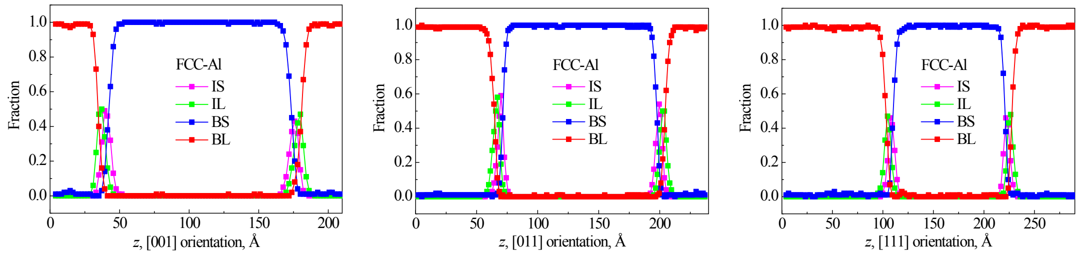


Figure S4. Three representative snapshots of FCC-Al with the CBS layer-wise profiles of atom number N_a; the density ρ; BOO parameters (i.e. q_4, q_6, w_4, and w_6); ABOO parameters (i.e. aq_4, aq_6, aw_4 and aw_6); coordinate number (CN); and Frenkel number (FN). Also exhibited are the fraction distributions of four atom types.

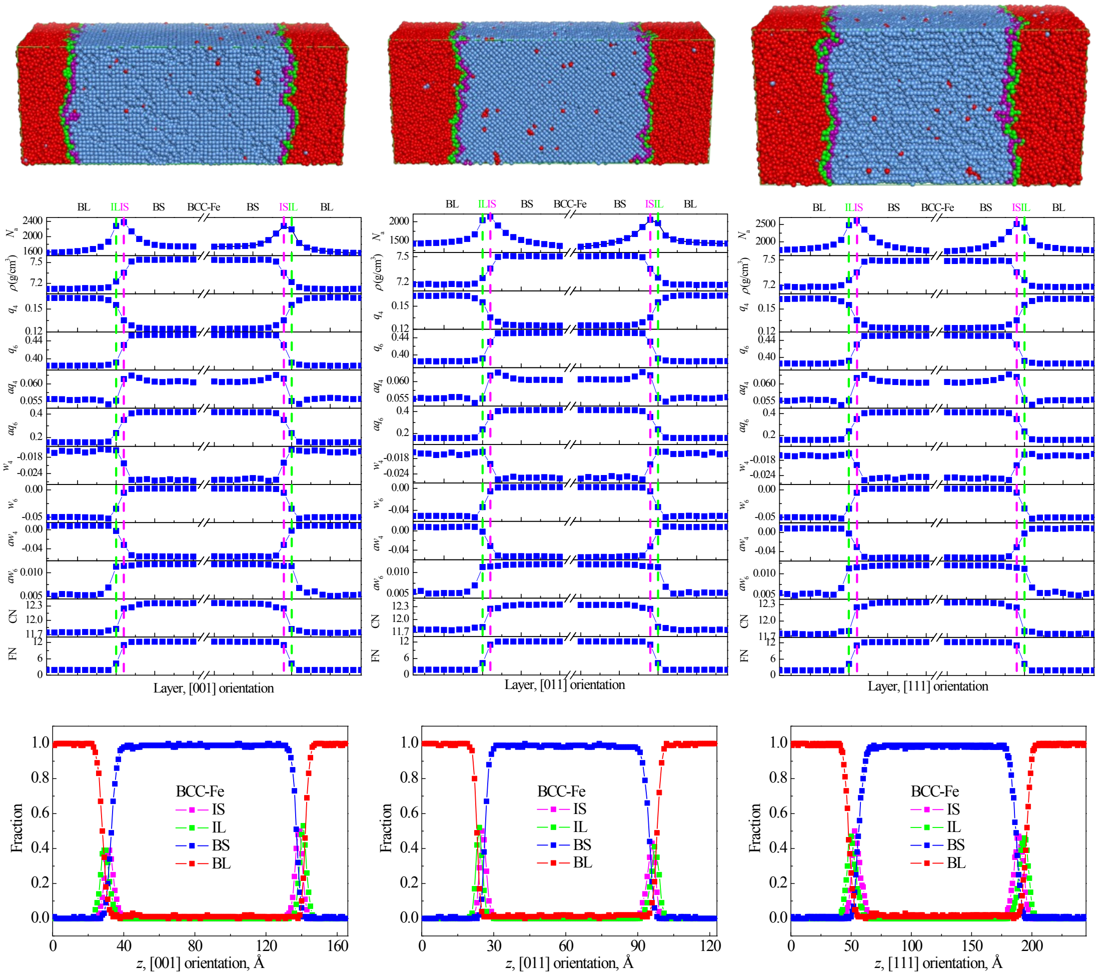


Figure S5. Three representative snapshots of BCC-Fe with the CBS layer-wise profiles of atom number N_a; the density ρ; BOO parameters (i.e. q_4, q_6, w_4, and w_6);

ABOO parameters (i.e. aq_4, aq_6, aw_4 and aw_6); coordinate number (CN); and Frenkel number (FN). Also exhibited are the fraction distributions of four atom types.

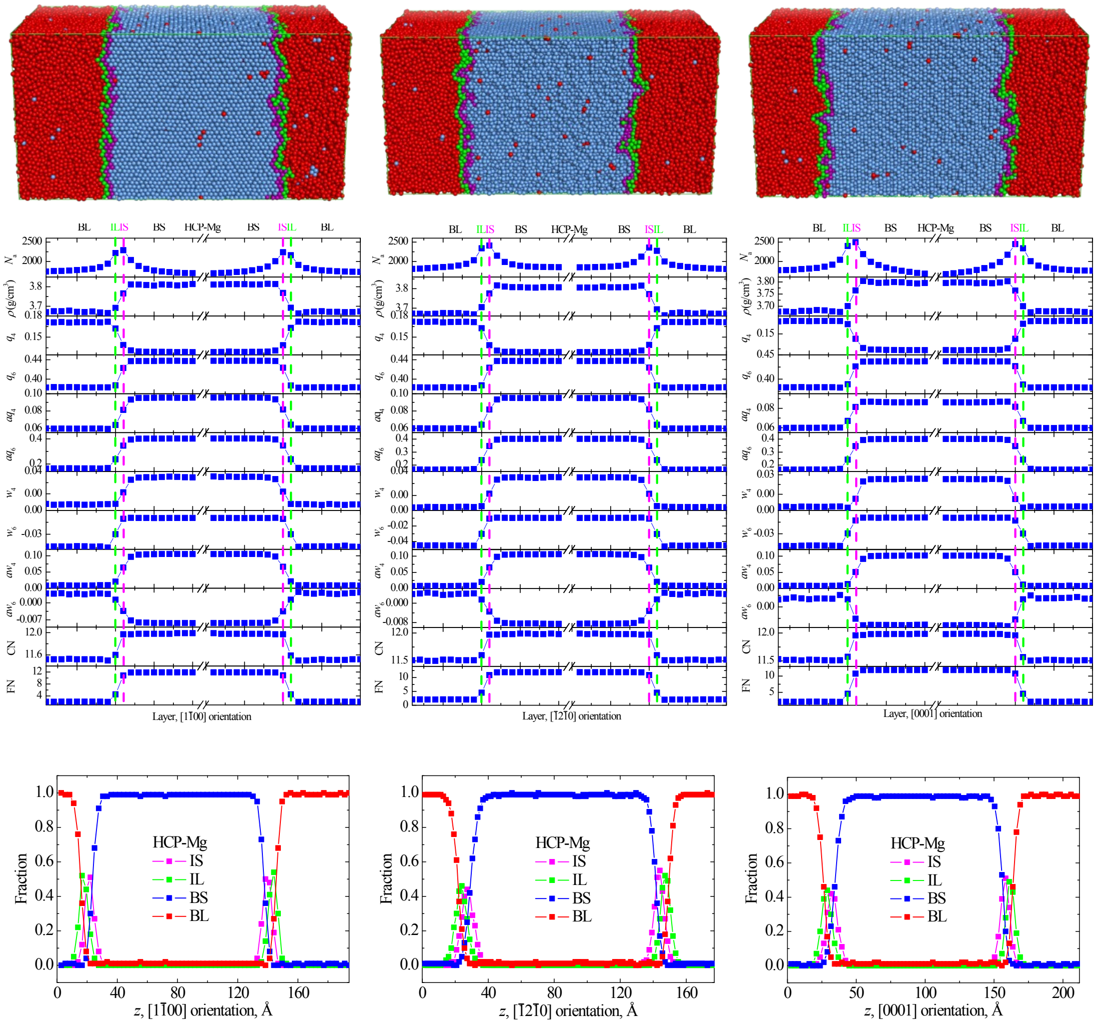


Figure S6. Three representative snapshots of HCP-Mg with the CBS layer-wise profiles of atom number N_a; the density ρ; BOO parameters (i.e. q_4, q_6, w_4, and w_6); ABOO parameters (i.e. aq_4, aq_6, aw_4 and aw_6); coordinate number (CN); and Frenkel number (FN). Also exhibited are the fraction distributions of four atom types.

ESTIMATION OF INTERFACIAL FREE ENERGY (IFE)

IFE of a SL interface can be defined as the free energy change to form an interface:

$$\gamma = \frac{\Delta F}{\Delta A} \tag{S1}$$

Where, γ is IFE, ΔF is the Helmholtz free energy excess, and ΔA is the area of the formed interface. For ΔF, we have:

$$\Delta F = \Delta p + \Delta K - T_{\mathrm{m}}\Delta S = \Delta p - T_{\mathrm{m}}\Delta S \tag{S2}$$

Because the kinetic energy $\Delta K = 0$ in equilibrium coexisting system (with uniform temperature), IFE is contributed by potential energy (PE) Δp and entropy (EN) $T_{\mathrm{m}}\Delta S$ terms: $\gamma = \frac{\sum(\langle \Delta f_i\rangle \cdot \langle n_i\rangle)}{\Delta A} = \frac{\sum((\langle \Delta p_i\rangle - \langle \Delta s_i\rangle \cdot T_{\mathrm{m}}) \cdot \langle n_i\rangle)}{\Delta A} = \gamma_{\mathrm{PE}} + \gamma_{\mathrm{EN}}$, where, $\gamma_{\mathrm{PE}} = \frac{\sum(\langle \Delta p_i\rangle \cdot \langle n_i\rangle)}{\Delta A}$ is the contribution of PE; $\gamma_{\mathrm{EN}} = \frac{\sum(-\langle \Delta s_i\rangle \cdot T_{\mathrm{m}} \cdot \langle n_i\rangle)}{\Delta A}$ is the contribution of EN; $\Delta f_i = f_i - f_{\mathrm{B}}$, $\Delta p_i = p_i - p_{\mathrm{B}}$, and $\Delta s_i = s_i - s_{\mathrm{B}}$ represent the differences, between i layer and the corresponding bulk phases, of atomic Helmholtz free energy, potential energy, and entropy, respectively; n_i is the atom number of i layer; the subscript i represents CBS layer L*i*, S*i*, IS or IL; and <…> means ensemble average.

So, according to the phase equilibrium, the entropy difference between BS and BL is the melting entropy:

$$\Delta s_{\mathrm{m}} = \Delta s_{\mathrm{BS \to BL}} = \frac{p_{\mathrm{BL}} - p_{\mathrm{BS}}}{T_{\mathrm{m}}} \qquad \text{(S3)}$$

Where, p_{BL} and p_{BS} are potential energies of bulk solid and bulk liquid, respectively. **Table S1** lists the PEs of bulk phases and corresponding melting entropies.

Table S1. The potential energies (PEs) and resulted melting entropies. The melting points are listed in **Table 2** in main text.

	FCC-Al			BCC-Fe			HCP-Mg		
	p_{BL}	p_{BS}	Δs_{m}	p_{BL}	p_{BS}	Δs_{m}	p_{BL}	p_{BS}	Δs_{m}
	eV/atom	eV/atom	meV/(atom·K)	eV/atom	eV/atom	meV/(atom·K)	eV/atom	eV/atom	meV/(atom·K)
[001] [0001]	-3.1519	-3.2588	0.1143	-3.6718	-3.8454	0.0951	-1.2863	-1.3794	0.1016
[011] $[1\bar{1}00]$	-3.1531	-3.2578	0.1113	-3.6738	-3.8417	0.0914	-1.2856	-1.3793	0.1024
[111] $[1\bar{2}10]$	-3.1530	-3.2566	0.1113	-3.6769	-3.8366	0.0869	-1.2869	-1.3793	0.1009

If we pre-set the entropy of BL as zero, the relative entropy of BS would be the negative melting entropy. As we know, the Frenkel number (FN) is used to distinguish solid and liquid atoms based on the symmetry of bonding environment coming originally from the 6-fold rotational symmetry. So, it calibrates to some extent the symmetry of the bonding configuration of an atom and subsequently its phase state. Therefore, we calibrate the relative entropies of IS and IL layers as proportional to FN for the intermediate interfacial layers as follow:

$$\Delta s_{\mathrm{IS}} = \Delta s_{\mathrm{BS}} \times \frac{\mathrm{FN(IS)} - \mathrm{FN(BL)}}{\mathrm{FN(BS)} - \mathrm{FN(BL)}}; \Delta s_{\mathrm{IL}} = \Delta s_{\mathrm{BS}} \times \frac{\mathrm{FN(IL)} - \mathrm{FN(BL)}}{\mathrm{FN(BS)} - \mathrm{FN(BL)}}$$

(S4)

Then, the entropy differences of IS and IL can be estimated as listed in **Table S2**.

Table S2. The ensemble-averaged FNs and the estimated entropy differences of four types of atoms relative to the pre-set zero entropy of BL, meV/(atom·K).

	Al				Fe				Mg			
	FN	Δs			FN	Δs			FN	Δs		
		[001]	[011]	[111]		[001]	[011]	[111]		[0001]	$[1\bar{1}00]$	$[1\bar{2}10]$
BS	11.94	-0.1143	-0.1113	-0.1113	12.25	-0.0951	-0.0914	-0.0869	11.87	-0.1016	-0.1024	-0.1009
IS	10.31	-0.0956	-0.0931	-0.0931	11.02	-0.0838	-0.0805	-0.0766	10.85	-0.0910	-0.0917	-0.0904
IL	3.52	-0.0178	-0.0173	-0.0173	4.27	-0.0218	-0.0209	-0.0199	4.52	-0.0252	-0.0254	-0.0251
BL	1.97	0	0	0	1.90	0	0	0	2.09	0	0	0

In above table, relative to the pre-set zero of entropy of BL, the rests of BS, IS, and IL are all negative. As for the entropy changes of BS→IS, and BL→IL listed in **Table S3**, the calculation equations are:

$$\Delta s_{\mathrm{BS\to IS}} = \Delta s_{\mathrm{IS}} - \Delta s_{\mathrm{BS}};\ \Delta s_{\mathrm{BL\to IL}} = \Delta s_{\mathrm{IL}} - \Delta s_{\mathrm{BL}} = \Delta s_{\mathrm{IL}} \tag{S5}$$

All $\Delta s_{\mathrm{BS\to IS}}$s are positive and all $\Delta s_{\mathrm{BL\to IL}}$s are negative, meaning, IS atoms are more disordered than their counterpart BSs and ILs are more ordered than their counterpart BLs.

Table S3. Entropy changes of BS→IS, and BL→IL, meV/(atom·K).

	Al			Fe			Mg		
	[001]	[011]	[111]	[001]	[011]	[111]	[0001]	$[1\bar{1}00]$	$[1\bar{2}10]$
$\Delta s_{\mathrm{BS\to IS}}$	0.0187	0.0182	0.0182	0.0113	0.0109	0.0103	0.0106	0.0107	0.0105
$\Delta s_{\mathrm{BL\to IL}}$	-0.0178	-0.0173	-0.0173	-0.0218	-0.0209	-0.0199	-0.0252	-0.0254	-0.0251

Then, the PE and EN contributions to IFE can be calculated based on the ensemble averages:

$$\gamma_{\mathrm{PE}} = \frac{\sum\left(\langle \Delta p_i \rangle \cdot \langle n_i \rangle\right)}{\Delta A};\ \gamma_{\mathrm{EN}} = \frac{\sum\left(-\langle \Delta s_i \rangle \cdot T_{\mathrm{m}} \cdot \langle n_i \rangle\right)}{\Delta A} \quad \text{(S6)}$$

Table S4 lists all data needed to calculate γ_{PE}. As shown in it, for liquid part, $\langle p_{\mathrm{L1}} \rangle_{\mathrm{s}}$ and $\langle p_{\mathrm{IL}} \rangle_{\mathrm{s}}$ of Al and Mg, as well as $\langle p_{\mathrm{L1}} \rangle_{\mathrm{s}}$ of Fe, almost equal to corresponding $\langle p_{\mathrm{BL}} \rangle_{\mathrm{s}}$, and only $\langle p_{\mathrm{IL}} \rangle_{\mathrm{s}}$ of Fe have a little drop relative to corresponding $\langle p_{\mathrm{BL}} \rangle_{\mathrm{s}}$; for solid part, all $\langle p_{\mathrm{S2}} \rangle_{\mathrm{s}}$ equal to corresponding $\langle p_{\mathrm{BS}} \rangle_{\mathrm{s}}$, and finally $\langle p_{\mathrm{IS}} \rangle_{\mathrm{s}}$ and $\langle p_{\mathrm{S1}} \rangle_{\mathrm{s}}$ have notable raises relative to corresponding $\langle p_{\mathrm{BS}} \rangle_{\mathrm{s}}$, especially $\langle p_{\mathrm{IS}} \rangle_{\mathrm{s}}$.

Table S4. Potential energy contribution to IFE from $\gamma_{\mathrm{PE}} = \frac{\sum\left(\langle \Delta p_i \rangle \cdot \langle n_i \rangle\right)}{\Delta A}$.

		$\langle p_i \rangle$, eV/atom							$\langle n_i \rangle$					ΔA, Å^2	γ_{PE}, mJ/m^2
		$\langle p_{\mathrm{BL}} \rangle$	$\langle p_{\mathrm{L1}} \rangle$	$\langle p_{\mathrm{IL}} \rangle$	$\langle p_{\mathrm{IS}} \rangle$	$\langle p_{\mathrm{S1}} \rangle$	$\langle p_{\mathrm{S2}} \rangle$	$\langle p_{\mathrm{BS}} \rangle$	$\langle n_{\mathrm{L1}} \rangle$	$\langle n_{\mathrm{IL}} \rangle$	$\langle n_{\mathrm{IS}} \rangle$	$\langle n_{\mathrm{S1}} \rangle$	$\langle n_{\mathrm{S2}} \rangle$		
Fe	[001]	-3.67	-3.68	-3.70	-3.79	-3.82	-3.84	-3.85	5100.34	6142.52	6351.39	5694.04	5172.92	20971.95	253.82
	[011]	-3.67	-3.68	-3.70	-3.79	-3.82	-3.84	-3.84	5521.00	6561.07	6777.92	6114.35	5527.80	23036.15	233.03
	[111]	-3.68	-3.68	-3.70	-3.79	-3.82	-3.83	-3.84	6736.39	8003.89	8278.01	7462.68	6755.28	28149.86	192.57
Al	[001]	-3.15	-3.15	-3.15	-3.21	-3.25	-3.26	-3.26	6291.93	6796.57	6771.98	6207.89	5773.70	35282.78	175.52
	[011]	-3.15	-3.15	-3.15	-3.22	-3.25	-3.26	-3.26	6552.77	7054.90	7095.88	6634.57	6317.28	37284.77	161.58
	[111]	-3.15	-3.15	-3.15	-3.22	-3.25	-3.25	-3.26	5682.54	6106.61	6146.67	5718.28	5399.88	32676.98	154.57
Mg	[0001]	-1.29	-1.28	-1.29	-1.35	-1.37	-1.38	-1.38	5705.03	6577.66	6680.21	5900.19	5398.49	37701.10	114.61
	$[1\bar{1}00]$	-1.29	-1.28	-1.29	-1.35	-1.38	-1.38	-1.38	9080.47	10285.43	10399.07	9272.30	8655.71	33444.15	153.36
	$[1\bar{2}10]$	-1.29	-1.28	-1.29	-1.35	-1.38	-1.38	-1.38	5142.38	5810.67	5897.31	5256.43	4895.23	33497.13	91.04

As for γ_{EN}, the FNs, as shown in **Figure S4~S6**, of all L*i* and S*i* layers, except IL and IS, have their own Bulk values. Only IL and IS deviate from the bulk references. Moreover, the positive $\Delta s_{\mathrm{BS} \to \mathrm{IS}}$ compensates largely the negative $\Delta s_{\mathrm{BL} \to \mathrm{IL}}$ as shown in **Table S3**, which reduced mostly the contribution of entropy to IFE. $\Delta s_{\mathrm{BS}\to\mathrm{IS}}$ and $\Delta s_{\mathrm{BL}\to\mathrm{IL}}$ in **Table S3**, $\langle n_i \rangle$ and ΔA in **Table S4**, and T_{m} in **Table 2** of main text provide all data for the estimation of γ_{EN}. **Table S5** lists the final results of γ_{PE}, γ_{EN}, and γ.

Table S5. The calculated PE and EN contributions to IFE, mJ/m^2.

Element	γ_{PE}			γ_{EN}			$\gamma = \gamma_{\mathrm{PE}} + \gamma_{\mathrm{EN}}$		
	[100] or [0001]	[110] or $[1\bar{1}00]$	[111] or $[1\bar{2}10]$	[100] or [0001]	[110] or $[1\bar{1}00]$	[111] or $[1\bar{2}10]$	[100] or [0001]	[110] or $[1\bar{1}00]$	[111] or $[1\bar{2}10]$
BCC-Fe	253.82	233.03	192.57	86.65	81.13	76.87	340.47	314.16	269.44
FCC-Al	175.52	161.58	154.57	-2.68	-3.41	-2.84	172.84	158.17	151.73
HCP-Mg	144.61	153.36	91.04	37.27	65.92	36.57	181.88	219.28	127.61