Understanding of magnetic behavior of the pseudo-binary $Co_{2-x}Ni_xZn_{11}$: in the light of crystal and electronic structures

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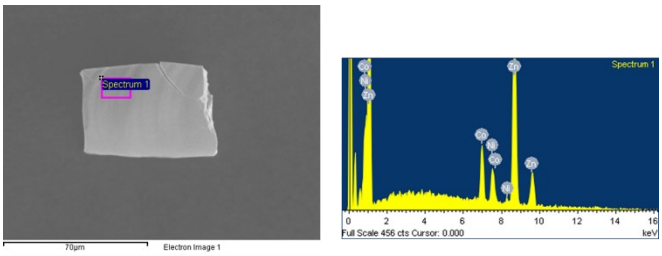
Supporting Information



(a) (b)

Fig. S1. (a) SEM image of the single crystal and (b) EDS spectrum of SC3 ($Co_{1.1}Ni_{0.9}Zn_{11}$).

Sample code	Loaded composition	Loaded composition (at. %)	EDS composition (at. %)
SC1	$Co_{1.7}Ni_{0.3}Zn_{11}$	$Co_{13.08}Ni_{2.30}Zn_{84.62}$	$Co_{13.10}Ni_{2.24}Zn_{84.66}$
SC2	$Co_{1.4}Ni_{0.6}Zn_{11}$	$Co_{10.77}Ni_{4.61}Zn_{84.62}$	$Co_{10.11}Ni_{4.40}Zn_{85.49}$
SC3	$Co_{1.1}Ni_{0.9}Zn_{11}$	$Co_{8.46}Ni_{6.92}Zn_{84.62}$	$Co_{8.32}Ni_{6.51}Zn_{85.17}$
SC4	$Co_{0.8}Ni_{1.2}Zn_{11}$	$Co_{6.15}Ni_{9.23}Zn_{84.62}$	$Co_{6.54}Ni_{9.72}Zn_{83.74}$
SC5	$Co_{0.5}Ni_{1.5}Zn_{11}$	$Co_{3.84}Ni_{11.54}Zn_{84.62}$	$Co_{3.42}Ni_{10.99}Zn_{85.59}$
SC6	$Co_{0.2}Ni_{1.8}Zn_{11}$	$Co_{1.53}Ni_{13.85}Zn_{84.62}$	$Co_{1.27}Ni_{13.04}Zn_{85.69}$

Table S1. Sample codes with their loaded composition and EDS composition.

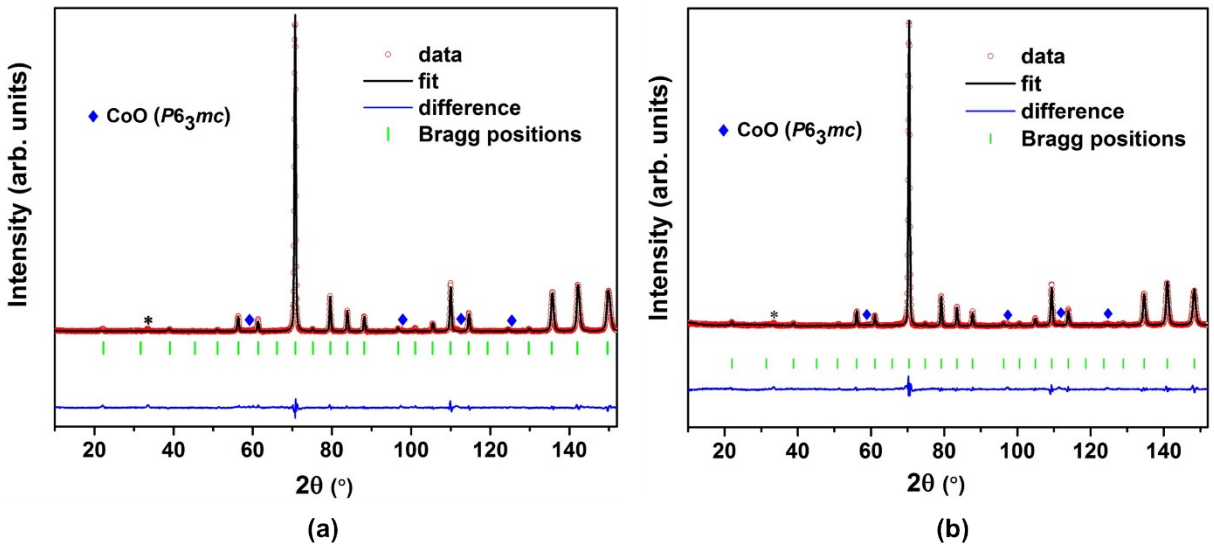
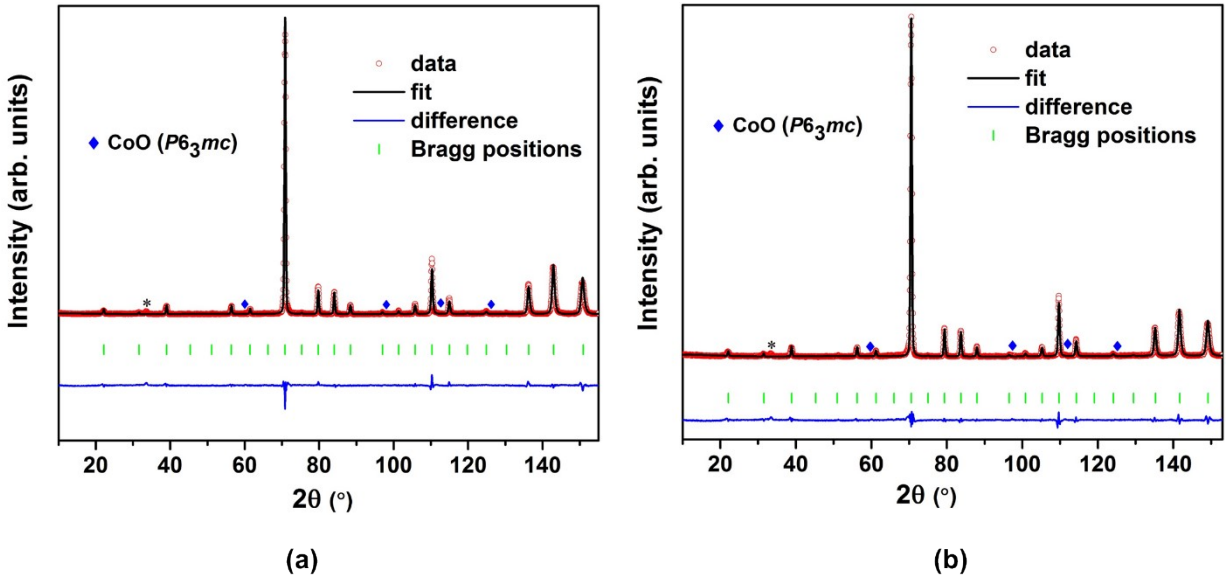


Fig. S2. Neutron powder diffraction data collected at (a) 3 K and (b) room temperature (300 K) for $Co_{1.1}Ni_{0.9}Zn_{11}$. The asterisks show ~0.5 % of λ/2 harmonics.

Fig. S3. Neutron powder diffraction data collected at (a) 3 K and (b) room temperature (300 K) for $Co_{0.5}Ni_{1.5}Zn_{11}$. The asterisks show ~0.5 % of λ/2 harmonics.



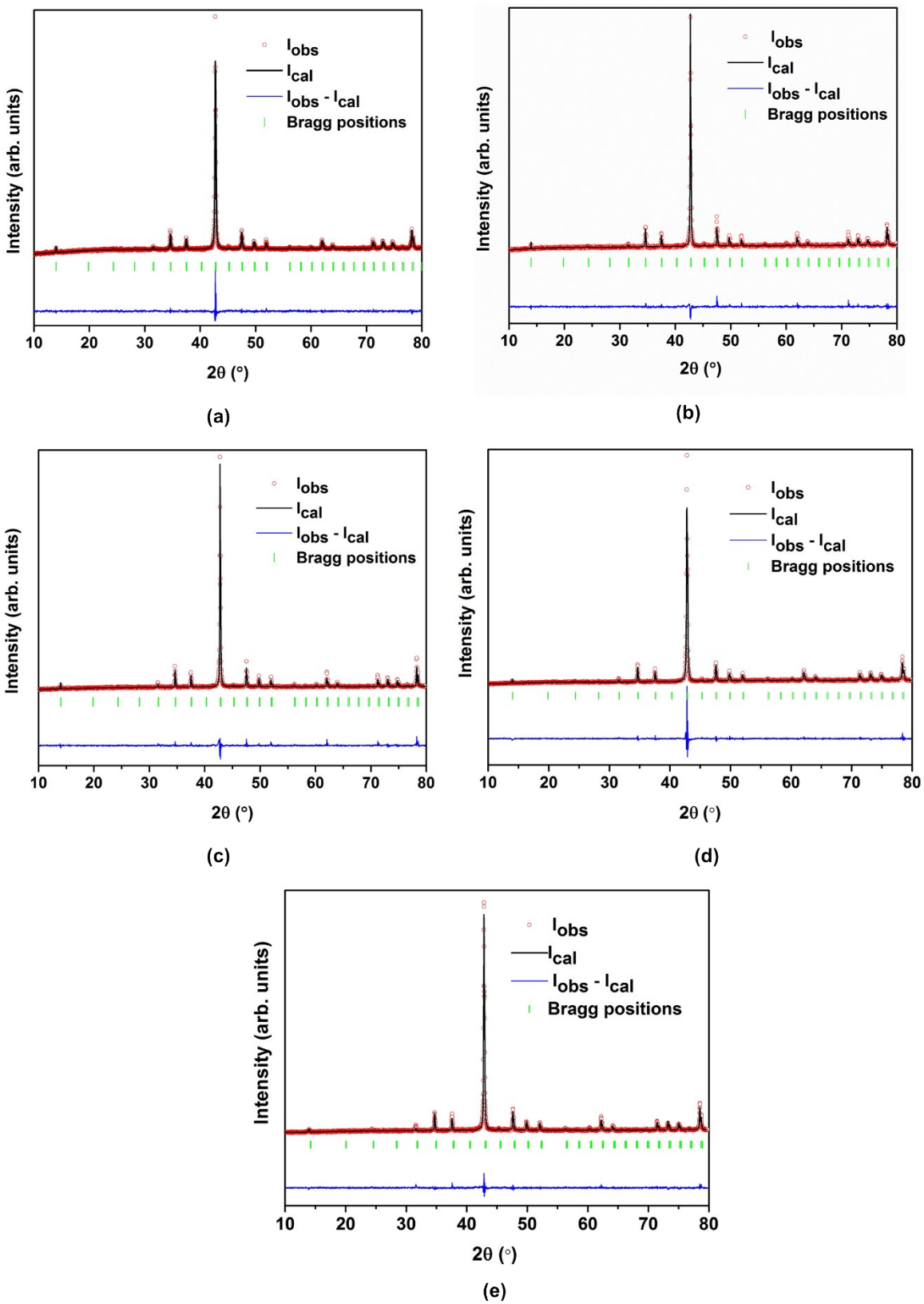


Fig. S4. Rietveld refinement plots for (a) $Co_{1.4}Ni_{0.6}Zn_{11}$, (b) $Co_{1.1}Ni_{0.9}Zn_{11}$, (c) $Co_{0.8}Ni_{1.2}Zn_{11}$, (d) $Co_{0.5}Ni_{1.5}Zn_{11}$, and (e) $Co_{0.2}Ni_{1.8}Zn_{11}$.

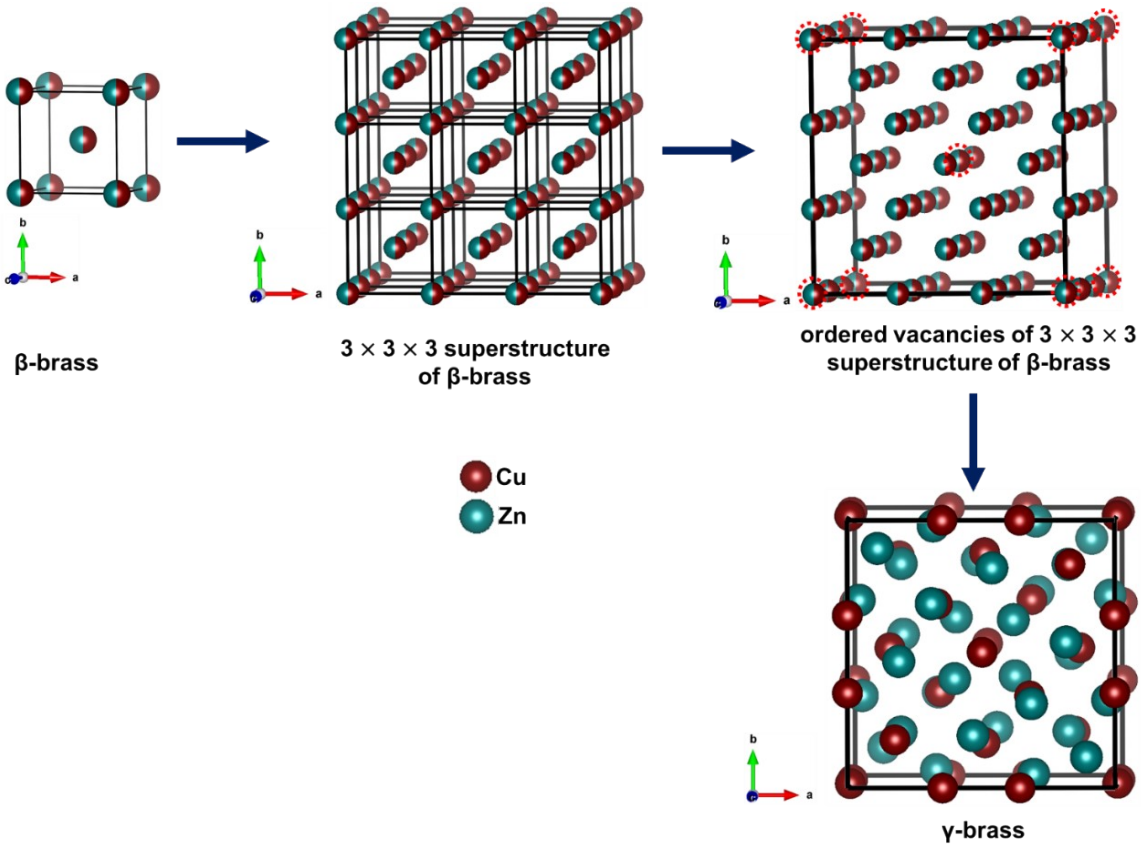


Fig. S5. Construction of γ-brass (Cu_5Zn_8) from β-brass (CuZn) structure.

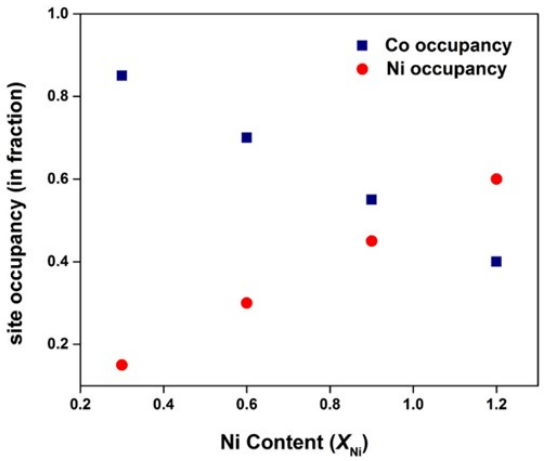


Fig. S6. Distribution pattern of Co and Ni at the OT (8*c*) site as a function of Ni content in $Co_{2-x}Ni_xZn_{11}$ suggested by SCXRD and EDS measurements.

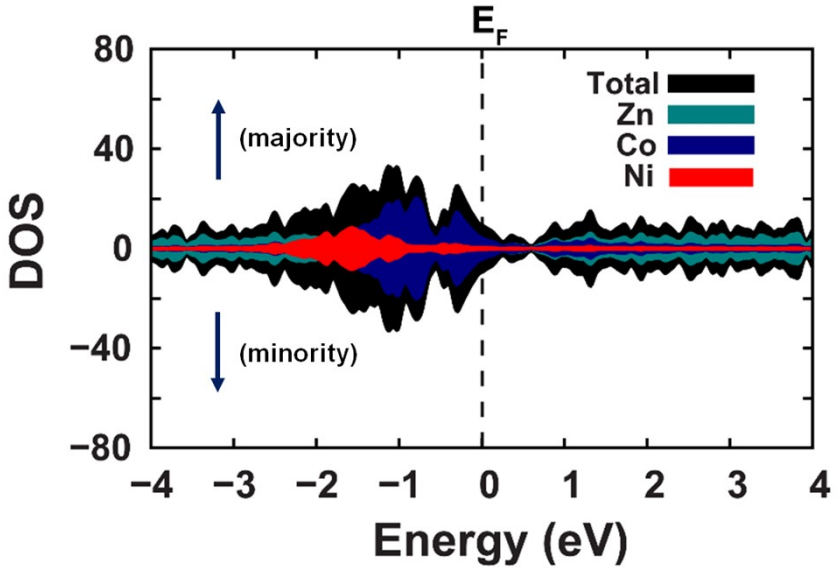


Fig. S7. DOS curve (majority and minority spin) of $Co_{1.5}Ni_{0.5}Zn_{11}$ pseudo-binary γ-brass compound in the Co–Ni–Zn system.

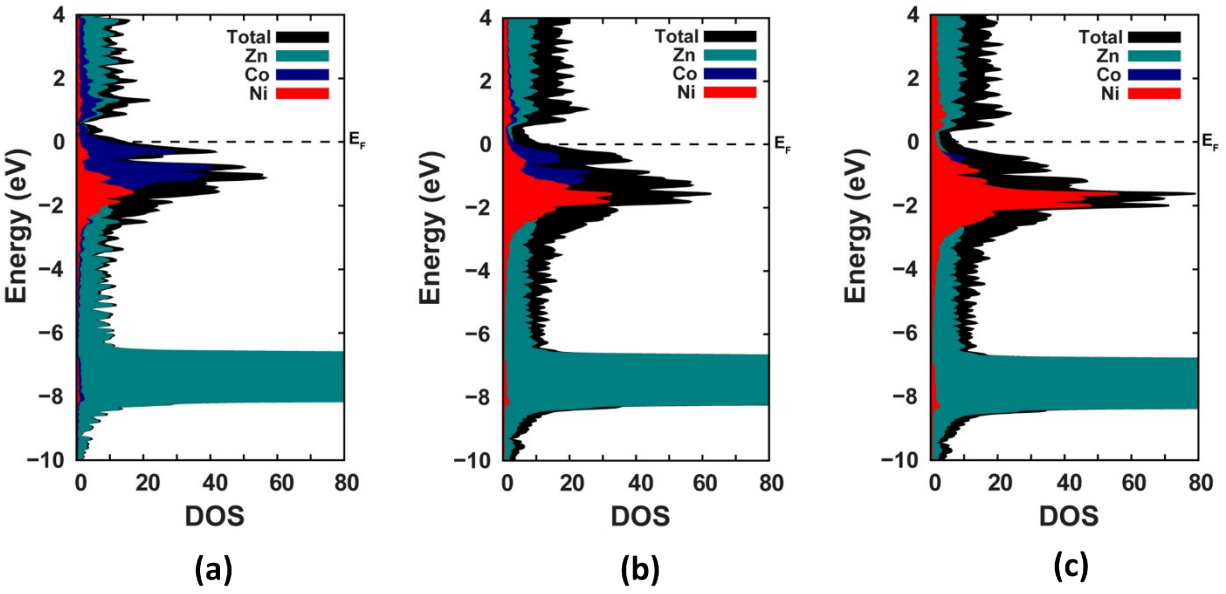


Fig. S8. DOS curves with the energy scale of –10 to +4 eV for (a) $Co_{1.5}Ni_{0.5}Zn_{11}$, (b) $Co_{1.0}Ni_{1.0}Zn_{11}$, and (c) $Co_{0.5}Ni_{1.5}Zn_{11}$.

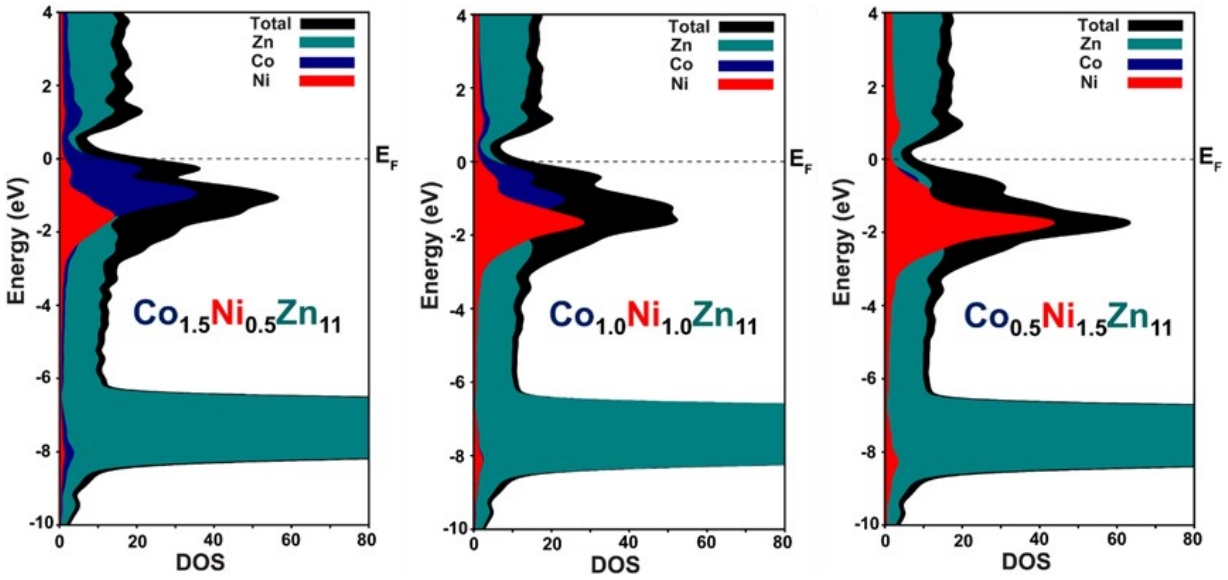


Fig. S9. Representation of total DOS by LOBSTER with the atom projected DOS: (left) "OT model" for $Co_{1.5}Ni_{0.5}Zn_{11}$, (middle) "OT model" for $Co_{1.0}Ni_{1.0}Zn_{11}$, and (right) "OT model" for $Co_{0.5}Ni_{1.5}Zn_{11}$.

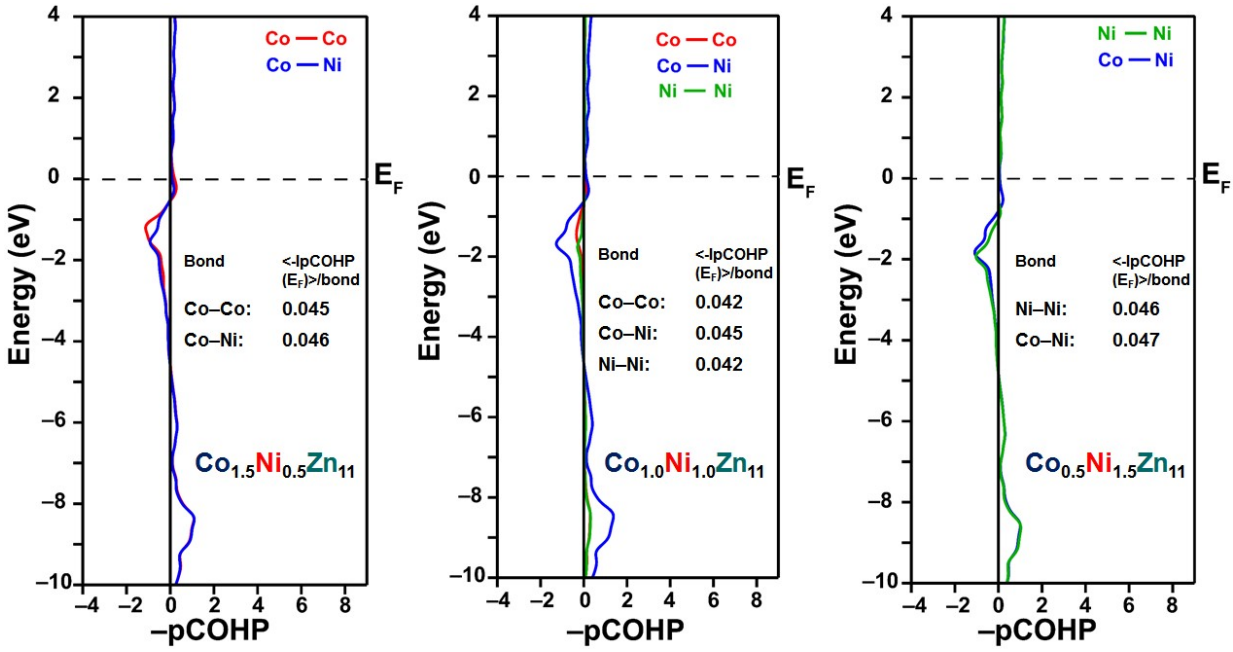


Fig. S10. COHP curves of OT—OT contacts for $Co_{1.5}Ni_{0.5}Zn_{11}$ (left), $Co_{1.0}Ni_{1.0}Zn_{11}$ (middle), and $Co_{0.5}Ni_{1.5}Zn_{11}$ (right).

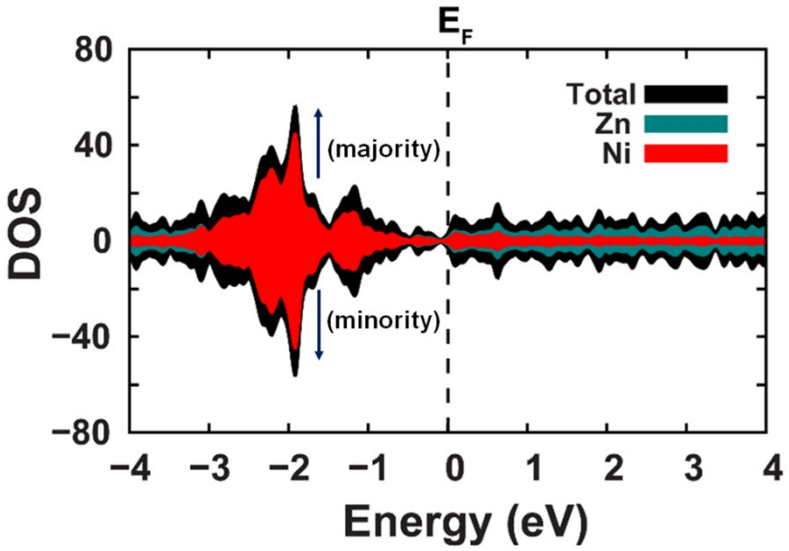


Fig. S11. DOS curve (majority and minority spin) of Ni_2Zn_{11} γ-brass compound.

Table S2. Interatomic distances and coordination polyhedron (< 3.5 Å) concerning each independent site of $Co_{1.1}Ni_{0.9}Zn_{11}$ compound.

Central atom	**Atoms**	**Interatomic distance (Å)**
Zn1 (IT)	3 Zn2	2.6051(6)
	3 Zn3	2.6137(5)
	3 Co/Ni	2.6239(6)
	3 Zn1	2.6425(6)
	Co/Ni	3.4800(6)
Co1/Ni1 (OT)	3 Zn3	2.5429(5)
	3 Zn3	2.5942(5)
	3 Zn1	2.6239(6)
	3 Zn2	2.7281(5)
	1 Zn1	3.4800(6)
Zn2 (OH)	2 Zn1	2.6051(6)
	1 Zn2	2.6160(8)
	2 Zn3	2.6196(4)
	2 Co/Ni	2.7281(5)
	4 Zn3	2.8107(5)
	2 Zn3	3.0065(5)
Zn3 (CO)	1 Co/Ni	2.5429(6)
	1 Co/Ni	2.5942(5)

1 Zn1	2.6137(5)
1 Zn2	2.6196(5)
4 Zn3	2.7241(5)
2 Zn2	2.8107(4)
1 Zn2	3.0065(5)
2 Zn3	3.2948(5)

Table S3. Site distribution of atoms in a 26-atom γ-cluster for each composition.

Composition of the model	**IT (8*c*)**	**OT (8*c*)**	**OH (12*e*)**	**CO (24*g*)**
$Co_{1.5}Ni_{0.5}Zn_{11}$	4Zn	3Co+1Ni	6Zn	12Zn
$Co_{1.0}Ni_{1.0}Zn_{11}$	4Zn	2Co+2Ni	6Zn	12Zn
$Co_{0.5}Ni_{1.5}Zn_{11}$	4Zn	1Co+3Ni	6Zn	12Zn

Section S1.

The formation energies for the model with composition $Co_{2-x}Ni_xZn_{11}$ have been evaluated using the following equation,

$$E_{Formation} = E_{Total} - Z \times [\ \{(2\text{-}x) \times E_{Co}\} + \{x \times E_{Ni}\} + \{11 \times E_{Zn}\}]$$

Where $E_{Formation}$ is the formation energy for the respective model. E_{Total} is the calculated total energy. Z is the formula unit (for γ-brass type phase, $Z = 4$). $E_{Co,}$ $E_{Ni,}$ and E_{Zn} are the total energies per atom for Co, Ni, and Zn respectively calculated using the stable allotropes of respective elements *e.g.* f.c.c. phase for Ni and the hexagonal phase for both Co and Zn.