1. Introduction

Intermetallic compounds feature unique bonding patterns compared to conventional metallic bonds, which makes this class of compounds challenging to deal with. They stimulate the interest of the researchers due to their compositional flexibility, structural complexity, and versatile physical and chemical properties. Complex intermetallics (CIMs) is a class of intermetallics that features large unit cells with ten to thousands of atoms, where the atoms in the unit cells constellate into a well-defined cluster. The CIMs are often associated with various kinds of disorders (substitutional, vacancy, positional disorder), that may have a profound impact on the physical and chemical properties of CIMs. Structural variation or phase stability of CIMs within a certain range is governed by (a) geometric factors indicating the ratio of atomic sizes, (b) valence electron concentration (vec), and (c) electronic effects including electronegativity. Their electronic structures often discern pseudo-gaps (state deficient regions) or small gaps across the Fermi level ($E_F$) in the density of states curves. Among numerous examples of CIMs, the \(\gamma\)-brass family is one of the well-known complex intermetallic compounds reported in the literature. Other than structural aspects of the \(\gamma\)-brass or \(\gamma\)-type compounds, their various physical and chemical properties such as mechanical, catalytic, transport, magnetic, etc., have been explored.

The ideal \(\gamma\)-brass type phases contain 52 atoms in their cubic unit cells of ~9–10 Å. Those 52 atoms are distributed into two 26-atom \(\gamma\)-cluster consisting of four concentric polyhedral shells. These four polyhedral shells are the inner tetrahedron (TT), the outer tetrahedron (OT), the octahedron (OH), and the distorted cuboctahedron (CO). The 26-atom clusters are located at two high symmetric points ((0, 0, 0) and (1/2, 1/2, 1/2)) of the cubic unit cell. These \(\gamma\)-brass phases are categor-
The stability of the $\gamma$-brass/$\gamma$-brass type phases is associated with the Hume-Rothery valence electron counting rule. The $\gamma$-brass/$\gamma$-brass type phases are stabilized at the $vec$ ($vec$ = average valence electrons per atom) of $21/13 \approx 1.62$, which appropriately relates to the group I $\gamma$-brass/$\gamma$-brass type compounds (s and p electrons are considered), though the compounds of this group exist over a range of $vec$. The $vec$ for the group II $\gamma$-brass type compounds is difficult as the assignment of the number of valence electrons in the 3d or 4d orbitals is challenging since partially filled 3d or 4d orbital is involved in the compounds of group II. Although the structure of many group II $\gamma$-brass/$\gamma$-brass type compounds is well established, their electronic structures and physical and chemical properties for several systems are yet to be fully explored.

In the cubic $\gamma$-brass/$\gamma$-brass type compounds, a pseudo-gap at the Fermi level ($E_F$) emerges in the density of states (DOS) curve, which induces phase stability of the aforementioned phases. The width of the pseudo-gap in the DOS curve which corresponds to the phase homogeneity range for a particular system, motivates us to extend the investigation from binary to pseudo-binary group II $\gamma$-brass type phases. In the recent past, Xie et al. investigated $\gamma$-brass type pseudo-binary phases in the Co–Zn–Pd and Fe–Zn–Pd systems starting from the binary $\gamma$-brass type phases in Co–Zn and Fe–Zn systems, respectively. They showed that Pd insertion into both the $\gamma$-brasses of Co$_2$Zn$_{11}$ and Fe$_2$Zn$_{11+\delta}$ is site-specific and the atomic distribution pattern in the structure has a profound effect on the magnetic properties of those phases. In the $\gamma$-brass type phase Co$_{2-x}$Zn$_{11-\delta}V_{y-x}$ ($V = \text{vacancy}$), stoichiometric Co$_2$Zn$_{11}$ shows Pauli-paramagnetic behavior, whereas it becomes Curie-Weiss paramagnetic with an increase in Co content. Due to Pd substitution for Co or Zn in the Co–Zn system, weak ferromagnetic (fermiagnetic) behavior appeared. Inspired by these previous studies, our investigation has been directed at the group II $\gamma$-brass type pseudo-binary phases having a mixture of magnetically active 3d elements.

A recent phase diagram in the ternary Ni–Co–Zn system suggests the presence of pseudo-binary phases between $\gamma$-Co$_2$Zn$_{21}$ and $\gamma$-Ni$_2$Zn$_{32}$, and assumed to form a continuous solid solution, though no crystallographic information is presented in this account. During this research program in the Ni–Co–Zn system, the pseudo-binary phases have been targeted via gradual substitution of Co by Ni (Co$_{2-x}$Ni$_{x}$Zn$_{11}$) and Zn by Ni (Co$_{x}$Ni$_{2-x}$Zn$_{11}$). In this contribution, we report a synthesis, crystal, electronic structures, and magnetic behavior of a series of $\gamma$-brass pseudo-binary phases loaded as Co$_{2-x}$Ni$_{x}$Zn$_{11}$ ($x = 0.3$–1.8).

2. Experimental section

2.1. Synthesis

Samples of loaded composition Co$_{2-x}$Ni$_{x}$Zn$_{11}$ ($x = 0.3$–1.8) were prepared from highly pure Co (99.998%, Alfa Aesar), Ni (99.995%, Alfa Aesar) and Zn (99.998%, Alfa Aesar). The precisely weighed constituent elements in ~300 mg scale were taken into 15 cm long one-end-closed quartz tubes. The open ends of the quartz tubes were then sealed under a high vacuum (~10$^{-5}$ mbar). The two-end sealed quartz tubes were kept inside the programmable chamber furnace. A temperature program was then set up for high-temperature synthesis. The furnace was first heated to 950 °C at a rate of 1.9 °C min$^{-1}$ and kept at that temperature for 17 h. Then, it was gradually cooled down to 450 °C at a rate of 0.2 °C min$^{-1}$, followed by annealing at this temperature for a period of 160 h. After that, the furnace was slowly cooled to 200 °C at a rate of 0.08 °C min$^{-1}$, and finally, the furnace was turned off and allowed to reach room temperature. The tubes were then taken out of the furnace and cut by a glass tube cutter. The obtained ingots were collected and crushed into small pieces with a mortar and pestle for further characterization.

For neutron powder measurements, three samples Co$_{2-x}$Ni$_{x}$Zn$_{11}$ ($x = 0.3$, 0.9, and 1.5) were prepared in ~3.5 g scale using the same temperature profile with longer annealing time (at 450 °C for 216 h).

2.2. Single crystal X-ray diffraction (SCXRD) data collection and processing

Under an optical microscope, crystals from the crushed ingots were selected and tested for diffraction experiments using a single-crystal X-ray diffractometer. Crystals were mounted on top of thin glass fiber using paratone oil, and diffraction intensities were collected at room temperature in a single crystal X-ray diffractometer equipped with graphite monochromatic Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å, 50 kV, 1.4 mA). Diffraction data were collected in a Bruker D8 QUEST PHOTON II detector. Apex III software was used to process and integrate the collected data. JANA2006 software was used to refine the structure. All the structural figures were drawn by VESTA software.

The crystallographic data of examined compositions (SC1–SC4) are also accessible as CIF files, which have been deposited to the Cambridge Crystallographic Data Centre, deposition numbers CCDC 2307991 (SC1), 2307993 (SC2) 2307992 (SC3), and 2307994 (SC4).

2.3. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) measurement

EDS measurements were done for both selected crystals from the samples and single crystals to analyze the elemental composition of the compounds. Smooth surfaces were selected...
and picked up on a stub coated with carbon tape. The measurement was performed in a Zeiss Evo 60 scanning electron microscope (SEM) equipped with an Evo-Oxford energy dispersive X-ray analyzer. Data were collected at several points with an accelerating voltage of 20 keV for 20 seconds. The EDS compositions for various loads have been given in Table S1.†

2.4. Powder X-ray diffraction (PXRD) measurement

PXRD measurements were performed to analyze the phases present in the synthesized samples. A small fraction of the crushed sample was taken in a mortar and ground with a pestle to a very fine powder. Powder samples were loaded and room-temperature X-ray diffraction data were collected using Bruker D2 phaser diffractometer in the 2θ range from 10° to 80°. JANA2006 software was used to perform refinements (le Bail and Rietveld) against the experimental diffraction patterns. The refinement quality was validated by R-values, difference curves, and goodness of fit (GOF) values. The experimental powder patterns were refined using the single-crystal refinement models to check the phase purity of the samples.

2.5. Neutron powder diffraction (NPD) measurement

Neutron diffraction patterns for those samples were collected at 3 and 300 K on the Echidna powder diffractometer (λ = 2.439532 Å) at the Australian Nuclear Science & Technology Organisation (ANSTO), Australia.35 The neutron diffraction patterns were analyzed by the Rietveld method using the JANA2006 software package.32,33

2.6. Computational details

The electronic structures of three model compositions (Co1.5Ni0.5Zn11, Co1.0Ni1.0Zn11, and Co0.5Ni1.5Zn11) were calculated using first-principles density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).36–38 All the calculations were carried out with Perdew–Burke–Ernzerhof (PBE) exchange–correlation (XC) functional in the framework of generalized gradient approximation (GGA)41 and projector augmented wave (PAW) method adopted for ion-electron interactions.42 The cut-off energy for the plane-wave basis was set to 520 eV and the energy tolerance criterion was set to 10⁻⁶ eV. All the structures were fully relaxed by the conjugate gradient (CG) algorithm until the interatomic forces were less than 0.01 eV Å⁻¹. A Monkhorst–Pack k-point mesh43 of 11 × 11 × 11 was used to sample the Brillouin zone for both geometry optimizations and static electronic structure calculations. The density of states (DOS) was calculated with and without spin-polarization with the projection of atomic orbitals of three elements (Co, Ni, and Zn) using the model composition. Detailed bonding analyses have been performed employing the LOBSTER program44–46 to calculate the projected crystal orbital Hamilton populations (pCOHP)47,48 implementing 3d, 4s, and 4p orbitals as the basis sets. The COHP curves have been plotted in Wxdragon.

2.7. Magnetic measurements

Magnetization was measured as a function of temperature and magnetic field for three samples, Co2x₋NiₓZn₁₁ (x = 0.3, 0.9, and 1.5) using a commercial vibrating sample magnetometer (VSM) (Quantum Design PPMS). Temperature-dependent magnetization was measured over 2.5–300 K under an applied magnetic field of 500 Oe. Isothermal magnetization measurements were performed at two temperatures of 2.5 and 300 K over H = ±9 T.

3. Results and discussion

3.1. Structural solution, refinement, and phase analysis

The crystal structure named ‘SC1’ (picked from the loading composition Co1.5Ni0.5Zn11) was solved by using superflip as implemented in JANA2006.32,33 The structure solution (in the space group I43m (no. 217)) generated four crystallographically independent sites (M1 (8c; x, x, x), M2 (8c; x, x, x), M3 (12c; x, 0, 0), and M4 (24g; x, x, z)). From the scattering factors of X-ray for Co (Z = 27), Ni (Z = 28), and Zn (Z = 30) are nearly similar, the accurate distribution of these atoms is difficult to determine based on electron density only. Initially, the positions were assigned according to the site occupancy pattern of the parent Co2Zn11. The ‘M2’ site was assigned to Co and other sites were assigned to Zn. Subsequent refinement converged at the R(obs) of 3.25%. To match the composition of the crystal SC1 (Co1.5Ni0.5Zn11) determined from the EDS analysis, the M2 site was modeled by partially substituting Ni for Co and the model was refined. At this stage, no significant residual electron density at the difference Fourier map was found. In the final stage of refinement, the anisotropic displacement parameters for all atomic sites were employed and the refinement resulted in R(obs) of 1.60% and GOF(all) of 1.22. The crystallographic data and refinement details are listed in Tables 1 & 2. The structural model obtained for SC1 was used to refine the single crystal X-ray data for the rest of the crystals namely SC2, SC3, and SC4 chosen from various loads. The SEM image and spectrum for SC3 are shown in Fig. S1.† The site occupancy factor (SOF) of the mixed M2 sites for SC1, SC2, SC3, and SC4 are fixed according to the compositional analyses shown in Table 2. The accurate site distribution patterns were further confirmed by neutron powder diffraction experiments. An isotropic extinction coefficient was employed at the final stage of refinement whenever necessary. Flack parameters were also refined to check the absolute configuration of the refined models. SC2 adopts the inverse configuration with respect to the other three crystals.

Due to the significant difference in scattering lengths of constituent elements (bCo = 2.49 fm, bNi = 10.3 fm, bZn = 5.68 fm), accurate site occupancy pattern in the structure of Co2₋₃NiₓZn₁₁, was determined by the neutron powder diffraction data refinements collected for the loading composition Co1.5Ni0.5Zn11. The neutron powder diffraction refinements confirmed the site mixing between Co and Ni atoms at the M2-
Table 1  Crystallographic data for SC1–SC4

<table>
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<th>SC1</th>
<th>SC2</th>
<th>SC3</th>
<th>SC4</th>
</tr>
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<td>Co₁₀Ni₆Zn₁₄</td>
<td>Co₁₀Ni₆Zn₁₄</td>
<td>Co₁₀Ni₆Zn₁₄</td>
</tr>
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<td>EDS formula (at%)</td>
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<td>Co₁₀Ni₆Zn₁₄</td>
<td>Co₁₀Ni₆Zn₁₄</td>
<td>Co₁₀Ni₆Zn₁₄</td>
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<td>Cubic</td>
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<td>I43m (217), 4</td>
<td>I43m (217), 4</td>
<td>I43m (217), 4</td>
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<td>a/Å</td>
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<td>8.9778(11)</td>
<td>8.9748(11)</td>
<td>9.0033(11)</td>
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<td>723.62(15)</td>
<td>722.90(15)</td>
<td>729.80(15)</td>
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<td>μ/cm⁻¹</td>
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<td>7.682</td>
<td>7.689</td>
<td>7.616</td>
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<td>Crystal color</td>
<td>Silvery with metallic luster</td>
<td>Four-circle diffractometer</td>
<td>Bruker Photon II</td>
<td>Mo-Kα</td>
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<td>Graphite</td>
<td>Multi-scan</td>
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<td>357</td>
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<td>T/K</td>
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<td>3.21–35.00</td>
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<td>3.2–36.21</td>
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<td>Rfactor</td>
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<td>No. of variables</td>
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<td>Observed reflections [I &gt; 3σ(I)]</td>
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<td>327</td>
<td>332</td>
<td>347</td>
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<td>R(F² &gt; 2σ(F²))</td>
<td>0.016</td>
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<td>0.014</td>
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<td>0.009</td>
<td>0.015</td>
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<td>GOF (all)</td>
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<td>Δρmin/Δρmax (e Å⁻³)</td>
<td>−0.50/0.73</td>
<td>−0.27/0.30</td>
<td>−0.41/0.69</td>
<td>−0.44/0.72</td>
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Table 2  Site distribution pattern for Co₂₋ₓNiₓZn₁₄ (x = 0.3, 0.6, 0.9, 1.2) phases

<table>
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<tr>
<th>Sample</th>
<th>Site</th>
<th>Atom</th>
<th>Wyck. site</th>
<th>Occupancy (SOF)</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Ucel [Å²]</th>
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</thead>
<tbody>
<tr>
<td>Co₀.₃Ni₆Zn₁₄</td>
<td>M1</td>
<td>Zn1</td>
<td>8c</td>
<td>1</td>
<td>0.39628(5)</td>
<td>x</td>
<td>x</td>
<td>0.01261(9)</td>
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<tr>
<td>M2</td>
<td>Co/Ni</td>
<td>8c</td>
<td>0.85/0.15</td>
<td>0.17229(5)</td>
<td>x</td>
<td>x</td>
<td>0.00900(9)</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>Zn2</td>
<td>12e</td>
<td>0.35407(8)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01231(11)</td>
<td></td>
</tr>
<tr>
<td>M4</td>
<td>Zn3</td>
<td>24g</td>
<td>0.30533(4)</td>
<td>x</td>
<td>0.95380(8)</td>
<td>0.01369(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>Zn1</td>
<td>8c</td>
<td>0.60388(3)</td>
<td>x</td>
<td>0</td>
<td>0</td>
<td>0.00881(5)</td>
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<tr>
<td>M2</td>
<td>Co/Ni</td>
<td>8c</td>
<td>0.82791(3)</td>
<td>x</td>
<td>x</td>
<td>0.00638(5)</td>
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<tr>
<td>M3</td>
<td>Zn2</td>
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<td>0.69425(2)</td>
<td>x</td>
<td>0.04671(3)</td>
<td>0.01109(6)</td>
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<tr>
<td>M1</td>
<td>Zn1</td>
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<td>0.39590(4)</td>
<td>x</td>
<td>x</td>
<td>0.01154(7)</td>
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<tr>
<td>M2</td>
<td>Zn1</td>
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<td>0.17203(4)</td>
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<td>Zn3</td>
<td>24g</td>
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<tr>
<td>M1</td>
<td>Zn1</td>
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<td>x</td>
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<td>0.01175(8)</td>
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<td>M2</td>
<td>Co/Ni</td>
<td>8c</td>
<td>0.17187(4)</td>
<td>x</td>
<td>x</td>
<td>0.00759(8)</td>
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<td>M3</td>
<td>Zn2</td>
<td>12e</td>
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<td>0</td>
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<td>0</td>
<td>0.01109(10)</td>
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<tr>
<td>M4</td>
<td>Zn3</td>
<td>24g</td>
<td>0.30621(3)</td>
<td>0.95405(5)</td>
<td>0.01247(8)</td>
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</table>

8c (OT) site (Table 3) and the composition obtained from the refinement (Co₀.₇₀Ni₀.₂₀Zn₁₄) is consistent with the composition determined by SEM-EDS measurements. The Rietveld plot for the NPD data analysis of Co₀.₇₀Ni₀.₂₀Zn₁₄ is shown in Fig. 1. An impurity of CoO (P6₃mc) has been found in the load while prepared for the large scale (~3.5 g). The low-temperature (3 K) powder NPD data indicated the absence of long-range magnetic ordering in the structure. The neutron powder diffraction patterns for the other two samples (Co₀.₃Ni₀.₇Zn₁₄; x = 0.9 and 1.5) are shown in Fig. S2 and S3.† The observed X-ray powder patterns for Co₀.₂₋ₓNiₓZn₁₄ pseudo-binary γ-brass type phases were refined using the simulated patterns from the single-crystal refinement model. For all six loading compositions of Co₀.₂₋ₓNiₓZn₁₄ (x = 0.3, 0.6, 0.9, 1.2, 1.5, and 1.8), no extra peak appears in the X-ray powder diffraction pattern which confirms the phase purity of...
the samples. Fig. 2 shows the PXRD patterns and Rietveld refinement plots for Co\textsubscript{1.7}Ni\textsubscript{0.3}Zn\textsubscript{11}. The PXRD patterns and Rietveld refinement plots of other loads (Co\textsubscript{2−x}Ni\textsubscript{x}Zn\textsubscript{11}; x = 0.6, 0.9, 1.2, 1.5, and 1.8) are shown in Fig. S4.†

Since the chemical hardness ($\eta$) of Ni ($\eta_{\text{Ni}} = 1.8$ eV) resembles that of Zn ($\eta_{\text{Zn}} = 1.6$ eV) and Co ($\eta_{\text{Co}} = 1.9$ eV). So, Ni has the flexibility to substitute both Co and Zn atoms in Co\textsubscript{2}Zn\textsubscript{11} $\gamma$-brass, and has formed an extended solid solution of pseudo-binary $\gamma$-brass Ni\textsubscript{2}Zn\textsubscript{11}–Co\textsubscript{2}Zn\textsubscript{11} in the Ni–Co–Zn ternary system.

### 3.2. Structural description

In general, the $\gamma$-brass structure is often described as a $3 \times 3 \times 3$ superstructure of $\beta$-brass with ordered vacancies at the body center and eight corners of the supercell of the body-centered cubic unit cell ($\beta$-brass) (Fig. S5†). The best way to rationalize the structure is to construct 26-atom $\gamma$-clusters located at two lattice points of a body-centered cubic unit cell ($I4_3m$). The 26-atom nested cluster consists of four polyhedral shells, their aggregation from inner to outer direction as follows: IT, OT, OH, and CO (the abbreviations are defined in the ‘Introduction section’) (Fig. 3). The structure of the pseudo-binary phases Co\textsubscript{2−x}Ni\textsubscript{x}Zn\textsubscript{11} is related to the structure of binary Co\textsubscript{2}Zn\textsubscript{11}–Ni\textsubscript{2}Zn\textsubscript{11} compounds. In the stoichiometric composition of the Co–Zn $\gamma$-brass type phase, i.e. Co\textsubscript{2}Zn\textsubscript{11}, the OT site is occupied by a minority constituent (Co), and the rest of the sites are occupied fully by Zn atoms, and the phase exists within the homogeneity range of 15.41 at% to 29.95 at% Co. Similarity, for the stoichiometric composition of Ni\textsubscript{2}Zn\textsubscript{11} in the $\gamma$-brass type phase in the Ni–Zn system, nickel (Ni)
occupies the OT site, and Zn atoms occupy the rest of the sites. The γ-brass type phase in the Ni–Zn system lies in the range of 15.41 at% to 21.15 at% Ni.11 In the structural model of Co2−xNiₓZn11, the IT, OH, and CO sites are completely occupied by Zn atoms and the OT site shows Co/Ni mixing. The coordination polyhedra and interatomic distances (cut off <3.5 Å) for each site are represented in Fig. 4 and Table S2,† respectively. Each site forms a pseudo-Frank–Kasper polyhedron. The distribution of Co and Ni at the OT site varies with the change in Ni concentration in Co2−xNiₓZn11 (Fig. S6†).

3.3. Electronic structures

First-principles DFT calculations have been performed to investigate the electronic structures for Co2−xNiₓZn11 (x = 0.5, 1.0, 1.5). Initially, spin-polarized magnetic calculations have been employed due to the presence of itinerant ferromagnets—Co and Ni in Co2−xNiₓZn11, however, the calculations resulted in a non-magnetic ground state (with a total magnetic moment of zero) as seen from the identical majority/minority DOS (Fig. S7†), which also supports our experimental results (see section 3.4). Thus, additional calculations have been performed considering the non-magnetic ground state. For Co1.5Ni0.5Zn11, four different models have been made to compare the preferable configuration. The relative formation energies for four different models have been calculated and the “OT model”, in which Zn resides on IT, OH, and CO sites, whereas Co and Ni are distributed over OT sites, has been found to possess the lowest energy. The formation energies for all the model structures were calculated against elemental Co, Ni, and Zn (section S1†). The relative formation energies for the respective models and the atomic distributions are listed in Table 4. The density of states (DOS) has been further calculated for all the respective models, and the DOS curve for the “OT model” is shown in Fig. 5a. The atom-projected DOS suggests the large contribution from the Co orbitals that originates just below the Fermi level (E_F) and propagates through the Fermi level until 0.3 eV where the first deep pseudo gap appears. This emphasizes the presence of partially filled Co orbitals. A substantial contribution comes from Ni orbitals relatively at a lower energy level. The Zn orbital remains dispersed with a strong d-peak at about (~7) to (~8) eV range (Fig. S8†).

As a reference to the “OT model” of the Co1.5Ni0.5Zn11, two other models with compositions Co1.0Ni1.0Zn11 and Co0.5Ni1.5Zn11 were built. For Co1.0Ni1.0Zn11, 2 Co and 2 Ni are placed at the OT site, and the rest of the sites are occupied by Zn. For Co0.5Ni1.5Zn11, 1 Co and 3 Ni at OT, and Zn at rest of the sites have been assumed. For both the compositions Co1.0Ni1.0Zn11 and Co0.5Ni1.5Zn11 (Fig. 5b and c), the DOS curves discern wide pseudo-gaps overshadowing of Co orbital contribution by Ni with the increase in Ni concentrations. Thus the high density at the Fermi level deteriorated to a wide

Table 4 Four representative models (with space group)51 based on the composition Co1.5Ni0.5Zn11 and their relative formation energy/cell (in eV)

<table>
<thead>
<tr>
<th>Model name</th>
<th>Space group</th>
<th>IT (8c)</th>
<th>OT (8c)</th>
<th>OH (12e)</th>
<th>CO (24g)</th>
<th>Relative formation energy/cell (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IT model</td>
<td>Cm</td>
<td>3Zn + 1Ni</td>
<td>3Co + 1Zn</td>
<td>6Zn</td>
<td>12Zn</td>
<td>1.1795</td>
</tr>
<tr>
<td>OT model</td>
<td>R3m</td>
<td>4Zn</td>
<td>3Co + 1Zn</td>
<td>6Zn</td>
<td>12Zn</td>
<td>0</td>
</tr>
<tr>
<td>OH model</td>
<td>P1</td>
<td>4Zn</td>
<td>3Co + 1Zn</td>
<td>5Zn + 1Ni</td>
<td>12Zn</td>
<td>0.8725</td>
</tr>
<tr>
<td>CO model</td>
<td>Cm</td>
<td>4Zn</td>
<td>3Co + 1Zn</td>
<td>6Zn</td>
<td>11Zn + 1Ni</td>
<td>1.9753</td>
</tr>
</tbody>
</table>

Fig. 3 (a) Representation of two 26-atom γ-clusters at Z (0, 0, 0) and H (1/2, 1/2, 1/2) in the structure of Co2−xNiₓZn11, (b) a 26-atom γ-cluster comprised of IT, OT, OH, and CO polyhedra.

Fig. 4 Coordination polyhedron around each Wyckoff site: (a) Zn1 (8c), (b) Co/Ni (8c), (c) Zn2 (12e), and (d) Zn3 (24g).
pseudo gap. In a previous report on γ-brass type compound Co2Zn11 (600 e\textsuperscript{-} /cell) by Xie et al., the DOS curve features two distinct pseudo-gaps: a narrow state-deficient region below the Fermi level (E\textsubscript{F}) (584 e\textsuperscript{-} /cell) and a broad pseudo gap above the E\textsubscript{F} with ∼604–608 e\textsuperscript{-} /cell.\textsuperscript{13} To investigate the electronic flexibility, a suitable element can be doped into Co2Zn11 γ-brass type compound by targeting a new ternary derivative, so that the Fermi level (E\textsubscript{F}) in the DOS curve of the γ-brass type Hume-Rothery phase would fall in the pseudo-gap.\textsuperscript{15} In our ongoing investigation, Ni has been chosen as a substituent for Co or Zn into Co2Zn11 as Ni has one additional d-electron than Co but two lesser valence electrons than Zn. In light of the occurrence of pseudo-gaps between 604 e\textsuperscript{-} /cell and 608 e\textsuperscript{-} /cell in the DOS curve of Co2Zn11, electronic structures of three different compositions Co2\textsubscript{x}Ni\textsubscript{1−x}Zn11 (x = 0.5, 1.0, and 1.5) have been checked. The DOS curve of the model system of Co1.5Ni0.5Zn11 is nearly similar to Co2Zn11 and shows two definite pseudo-gaps (605.2 e\textsuperscript{-} and 607.7 e\textsuperscript{-} /cell) above the Fermi level (E\textsubscript{F}) (602 e\textsuperscript{-} /cell) and a narrow pseudo-gap (583.9 e\textsuperscript{-} /cell) below E\textsubscript{F} (Fig. 5a). For the composition Co1.0Ni1.0Zn11 (604 e\textsuperscript{-} /cell) and Co0.5Ni1.5Zn11 (606 e\textsuperscript{-} /cell) (Fig. 5b and c), the Fermi level (E\textsubscript{F}) lies at the wide pseudo-gap in the DOS curves. Furthermore, the VASP projection of the atomic orbitals are compared with the LOBSTER projection (Fig. S9). The composition with electrons of 584 e\textsuperscript{-} /cell is expected to be achieved by the substitution of Zn sites by Ni in γ-Co–Ni–Zn, i.e. Co2Zn0.5Ni2. Hence, to adjust the total valence electron count of 584 e\textsuperscript{-} /cell in γ-brass type Co0.5Ni1.5Zn11, our immediate goal is to target ternary derivative by considering Ni substitution for Zn sites.

### 3.3.1. Bonding analysis

The COHP curves for all near neighbor inter- and intra-atomic contacts have been considered (<3 Å). Two distinct pseudo-gaps located around 0.3 and 0.7 e\textsuperscript{-} above the Fermi level in the DOS curve for Co1.5Ni0.5Zn11 is noticed, which can be correlated to the crossover between bonding and non-bonding/anti-bonding states of OT(Co/Ni)–OH(Zn) bond at ∼0.3 e\textsuperscript{-} and OT(Co/Ni)–IT(Zn) and OT(Co/Ni)–CO(Zn) bonds around 0.7 e\textsuperscript{-} (Fig. 6). The broad pseudo-gaps near E\textsubscript{F} in the DOS curves of Co2\textsubscript{x}Ni\textsubscript{1−x}Zn11 (x = 1.0, 1.5), are the evidences of optimization of Co/Ni–Zn contacts as the crossover points gradually shifts towards the Fermi level upon increasing Ni content (Fig. 7 and 8).

The Co–Zn and Ni–Zn interatomic contacts for all the cases exhibit bonding interaction throughout the whole energy range, while Zn–Zn intra-atomic contacts show primarily bonding interactions alongside an anti-bonding peak appears around 7 e\textsuperscript{-} below the E\textsubscript{F} due to d–d overlapping interactions. That’s why the average negative integrated pCOHP (–\langle IpCOHP\rangle) value for Co–Zn and Ni–Zn hetero-atomic contacts is higher than that of Zn–Zn homo-atomic contacts. In addition, the average bond strength for Co–Zn is higher as compared to Ni–Zn contacts which signifies the strong bonding interaction between them. Though homoatomic Zn–Zn contacts are the weakest, due to the highest populations, they contribute more than 60% towards the overall stability. As the Ni content gradually increases, the contribution for Ni–Zn dominates over Co–Zn contacts (Table 5). The homoatomic interaction between transition elements [(M⋯M) ≈ 4.72 Å; M = Co and Ni] discerns very weak/non-bonding interaction in the COHP curves (Fig. S10†). Moreover, the valence electron concentration per atom for the three compositions is approximately 11.6, close to the vec of copper atoms. In the non-spin polarised electronic structures of copper, the Cu–Cu non-bonding states at E\textsubscript{F} in the COHP is a sign of non-magnetic behavior (diamagnetism in practice).\textsuperscript{52} A similar feature (non-bonding/very weak
bonding) of M⋯M in the COHP curves reveals non-magnetic behavior in Co$_{2-x}$Ni$_x$Zn$_{11}$ ($x = 0.5$, 1.0, and 1.5).

3.4. Magnetic properties and correlation from DOS

The magnetic susceptibility ($\chi$) for three samples in the pseudo-binary $\gamma$-brass type phases of Co$_{2-x}$Ni$_x$Zn$_{11}$ ($x = 0.3$, 0.9, and 1.5) was measured at 500 Oe magnetic field and iso-thermal magnetization data was collected at two different temperatures of 2.5 and 300 K up to the external field of 9 T.

The $M(H)$ curves of Co$_{1.7}$Ni$_{0.3}$Zn$_{11}$ show the total contributions coming from both paramagnetic (PM) (linear in $H$ and having a positive slope) and ferromagnetic (FM) term that gives a quick rise of the magnetization close to $H = 0$. The FM contribution may arise due to some cobalt-rich regions or a
minute impurity of the pure cobalt phase (cobalt has a high Curie temperature \(T_c\) of about 1400 K). Nevertheless, the isothermal magnetization \(M(H)\) curves at two measured temperatures do not show any saturation even at a very high magnetic field of 9 T, suggesting the dominating paramagnetic behavior of the Co1.7Ni0.3Zn11 compound (Fig. 9b). To extract the FM and PM contributions in \(M(H)\) curve, the following eqn (1) can be used:\(^{53}\)

\[
M(H) = \frac{2M_{FM}^2}{\pi} \tan^{-1}\left(\frac{H + H_c}{H_c\tan\left(\frac{\pi M_{FM}^R}{2M_{FM}^P}\right)}\right) + \chi H \tag{1}
\]

The first part defines the ferromagnetic term (saturation magnetization: \(M_{FM}^S\), intrinsic coercivity: \(H_c\), and remanent magnetization: \(M_{FM}^R\)) and the second part represents the linear component coming from the paramagnetic term. The inset of Fig. 9b demonstrates the fitted of the experimental data recorded at 300 K in the \(M(H)\) plot. The parameters obtained from fitting are \(M_{FM}^S = 0.01337\) emu g\(^{-1}\), \(H_c = 32.4\) Oe, \(M_{FM}^R = 0.00559\) emu g\(^{-1}\), and \(\chi = 3.25 \times 10^{-7}\) emu per Oe-g. From the saturation magnetization value of \(0.14 \times 10^{-3}\) \(\mu_B\) obtained from the impure cobalt source and saturation of cobalt metal of \(1.74\) \(\mu_B\),\(^{54}\) we calculate the relative impure cobalt amount to be approximately 0.008 mol%, which is eventually beyond the scope of detection from powder diffraction measurements.

The maximum value of magnetization that we achieved at 9 T for 300 and 2.5 K is \(4.16 \times 10^{-2}\) and \(4.41 \times 10^{-2}\) emu g\(^{-1}\), respectively. A monotonic decay of the magnetic susceptibility \(\chi = \frac{M}{H}\) was observed with the increase of the temperature from 2.5 to 300 K (Fig. 9a). The susceptibility varies from \(\sim 8.0 \times 10^{-6}\) to \(28.5 \times 10^{-6}\) emu per Oe-g with temperature from 300 to 2.5 K.

The nature of the \(M(H)\) curves (at 300 and 2.5 K) for Co1.1Ni0.9Zn11 are quite complicated (Fig. 10). At first, \(M\) increases with increasing \(H\), by attaining a maximum value of \(1.2 \times 10^{-3}\) and \(10.67 \times 10^{-3}\) emu g\(^{-1}\) at the magnetic field of 0.41 and 1.65 T respectively, then slightly decreases and \(M\) becomes zero at \(\sim 1.7\) and 6.8 T for 300 and 2.5 K, respectively. On further increase in \(H\), the \(M\) decreases linearly to reach a maximum negative magnetization value of \(-16.3 \times 10^{-3}\) and \(-6 \times 10^{-3}\) emu g\(^{-1}\) at \(H = 9\) T for 300 and 2.5 K, respectively, which predominately indicates the diamagnetic behavior of the Co1.1Ni0.9Zn11 compound. At the window of \(\pm 500\) Oe, the \(M(H)\) plot illustrates a quick upturn suggesting also ferromagnetic contribution from an impurity of the cobalt phase. So, the \(\chi\) vs. \(T\) plot at 500 Oe magnetic field also shows a gradual decay of the susceptibility value up to 300 K (Fig. 10).

\[
\text{Table 5: The (IpCOHP (\(E_f\))) per bond and IpCOHP (\(E_f\)) contribution of hetero- and homo-atomic contacts for three compositions}
\]

<table>
<thead>
<tr>
<th>Bonds</th>
<th>No. of bonds</th>
<th>IpCOHP ((E_f)) per bond</th>
<th>IpCOHP ((E_f)) contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1.5Ni0.5Zn11</td>
<td>Co–Zn 72</td>
<td>2.09</td>
<td>29.89</td>
</tr>
<tr>
<td></td>
<td>Ni–Zn 24</td>
<td>1.94</td>
<td>9.27</td>
</tr>
<tr>
<td></td>
<td>Zn–Zn 186</td>
<td>1.65</td>
<td>60.84</td>
</tr>
<tr>
<td>Co1.0Ni1.0Zn11</td>
<td>Co–Zn 48</td>
<td>2.10</td>
<td>19.51</td>
</tr>
<tr>
<td></td>
<td>Ni–Zn 48</td>
<td>1.95</td>
<td>18.18</td>
</tr>
<tr>
<td></td>
<td>Zn–Zn 198</td>
<td>1.62</td>
<td>60.31</td>
</tr>
<tr>
<td>Co0.5Ni1.5Zn11</td>
<td>Co–Zn 24</td>
<td>2.10</td>
<td>9.68</td>
</tr>
<tr>
<td></td>
<td>Ni–Zn 72</td>
<td>1.96</td>
<td>27.04</td>
</tr>
<tr>
<td></td>
<td>Zn–Zn 204</td>
<td>1.62</td>
<td>63.28</td>
</tr>
</tbody>
</table>
In addition, Pt<sub>2</sub>Zn<sub>11</sub><sub>−</sub><sub>δ</sub> (0.2 &lt; δ &lt; 0.3) also shows similar diamagnetic behavior with the magnetic susceptibility of −3.3 × 10<sup>−8</sup> emu per Oe-g to −3.9 × 10<sup>−8</sup> emu per Oe-g.<sup>25</sup>

As seen in Fig. 11, the $M$ vs. $H$ graph for Co<sub>0.5</sub>Ni<sub>1.5</sub>Zn<sub>11</sub> illustrates a complete diamagnetic nature of the compound at 300 K even at the very low field of 500 Oe. The diamagnetic susceptibility seems to remain almost unchanged from 150 to 300 K as shown in $\chi$ vs. $T$ plot (Fig. 11a). Interestingly, it is clear that the ferromagnetic impurity due to the pure cobalt phase is diminished as the cobalt content is gradually decreased in the measured compounds, Co<sub>2−x</sub>Ni<sub>x</sub>Zn<sub>11</sub> ($x$ = 0.3, 0.9, 1.5).

So, overall, we say that a low Ni content ($x$ = 0.3) in the Co<sub>2−x</sub>Ni<sub>x</sub>Zn<sub>11</sub> shows paramagnetic behavior, whereas $x$ = 1.5 (the end measured compound, Co<sub>0.5</sub>Ni<sub>1.5</sub>Zn<sub>11</sub>) exhibits diamagnetism. The change in magnetism of Co<sub>2−x</sub>Ni<sub>x</sub>Zn<sub>11</sub> can be demonstrated from the viewpoint of the magnetic behavior of the substitutional alloys (e.g. Ni<sub>1−x</sub>Cu<sub>x</sub>).<sup>55</sup> The magnetic behavior of the compounds in Co<sub>2−x</sub>Ni<sub>x</sub>Zn<sub>11</sub> can be represented as a linear function of two terms: $M_{\text{total}} = aM_{\text{para}} + (1 - a)M_{\text{dia}}$; where, ‘$a$’ and ‘$(1 - a)$’ stand for the coefficient corresponding to the paramagnetism and diamagnetism respectively, and the value of ‘$a$’ is deeply linked with Ni-concentration ($x_{\text{Ni}}$), $M_{\text{para}}$ is the magnetization due to paramagnetism (positive), and $M_{\text{dia}}$ is the magnetization due to diamagnetism (negative). As Ni content is gradually increased, Ni atoms replace Co atoms at the OT sites in the $\gamma$-cluster. As the Ni-rich pseudo-binary compound Co<sub>0.5</sub>Ni<sub>1.5</sub>Zn<sub>11</sub> exhibits the diamagnetic behavior, diamagnetism is expected in the binary $\gamma$-brass type Ni<sub>2</sub>Zn<sub>11</sub>. Moreover, the spin-polarization DOS (majority and minority
spin) calculations for the Ni\textsubscript{2}Zn\textsubscript{11} \(\gamma\)-brass compound show a very low density of states at the Fermi level, and symmetrical majority and minority spin contribution in the Ni-projected DOS curve (Fig. S1†). These may be an indication of the diamagnetic behavior of the Ni\textsubscript{2}Zn\textsubscript{11} \(\gamma\)-brass compound, though experimental validation is yet to be pursued. The composition-dependent magnetism is also noticed in the \(\gamma\)-brass type phase of the binary Co–Zn system. Pauli paramagnetic behavior of 15.4 at% Co–Zn switches to the Curie–Weiss paramagnetism, while the increase of Co concentration in \(\gamma\)-brass type Co–Zn phase (24.86 at% Co).\(^{13}\)

From DOS curves, it is clear that the density of states near the vicinity of the Fermi level \((E_F)\) gradually decreases from the model composition of Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} to Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11} as the Ni concentration increases in Co\textsubscript{2–x}Ni\textsubscript{x}Zn\textsubscript{11} (Fig. 5). The density of states at the \(E_F\) is \(~16\) states per eV per cell for Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} and \(~7\) states per eV per cell for Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11}. Among two magnetically active elements (Co and Ni), the major contribution at the Fermi level comes from the orbitals of Co rather than Ni in Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11}. The contribution of Co atoms is more significant for Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11} and Co\textsubscript{1.0}Ni\textsubscript{1.0}Zn\textsubscript{11}; and drops down to the higher Ni content phases in Co\textsubscript{2–x}Ni\textsubscript{x}Zn\textsubscript{11}.

The magnetism of three studied pseudo-binary \(\gamma\)-brass type phases in the Co–Ni–Zn system (low Ni-content to intermediate Ni-content in Co\textsubscript{2–x}Ni\textsubscript{x}Zn\textsubscript{11}) can alternatively be rationalized highlighting the ordered compositions, where the number of Co atoms/cell decrease from 6 to 2 atoms/cell at OT site (Table S3†) from Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} to Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11}. The Stoner criterion\(^{56}\) gives an approximate idea about the magnetism of an itinerant magnet, while \(I \times N(E_F) > 1\), the metals or alloys exhibit ferromagnetism, where, \(I\) is a measure of the strength of magnetic exchange interaction in metals and \(N(E_F)\) is the density of states at the Fermi level \((E_F)\). However, \(“I”\) depends on the local environment of the magnetically active elements under the assumed system,\(^{57}\) here the \(I\) values are taken from the literature. For Co and Ni, the \(I\) values are 0.49 eV and 0.50 eV, respectively.\(^{58}\) Moving from low Ni content (Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11}) to intermediate Ni content (Co\textsubscript{1.0}Ni\textsubscript{1.0}Zn\textsubscript{11}) phase, the density of states at the Fermi level per Co atoms \((N(E_F)_{Co})\) varies from 1.49 eV\(^{-1}\) to 1.06 eV\(^{-1}\), and for high Ni content phase (Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11}) the density of states at the Fermi level per Ni atoms, \((N(E_F)_{Ni})\), reveals 0.23 eV\(^{-1}\) in the unit cell as calculated from projected DOS curve for the respective model compositions (Fig. 5). Applying the Stoner condition under the first approximation, \([I \times N(E_F)]_{Co}\) product is 0.73 and 0.52 for Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} and Co\textsubscript{1.0}Ni\textsubscript{1.0}Zn\textsubscript{11}, respectively and \([I \times N(E_F)]_{Ni}\) equals to 0.12 for Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11}. Since the significant contribution at the Fermi level \((E_F)\) for Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} and Co\textsubscript{1.0}Ni\textsubscript{1.0}Zn\textsubscript{11} is mainly due to Co atoms, and for Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11} is due to the Ni atoms, \((N(E_F)_{Co})\) have been taken for the Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} and Co\textsubscript{1.0}Ni\textsubscript{1.0}Zn\textsubscript{11} compositions into consideration and \((N(E_F)_{Ni})\) for the Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11}. From the \(I \times N(E_F)\) value, the magnetism of Co\textsubscript{1.0}Ni\textsubscript{1.0}Zn\textsubscript{11} is expected to be paramagnetic,\(^{59}\) while the value of the \(I \times N(E_F)\) for Co\textsubscript{1.5}Ni\textsubscript{0.5}Zn\textsubscript{11} and Co\textsubscript{0.5}Ni\textsubscript{1.5}Zn\textsubscript{11} is too small that the expected to show nonmagnetic behavior.\(^{58}\)

(pd substitution in Co–Zn \(\gamma\)-brass type phase yields two pseudo-binary Co\textsubscript{0.9}Pd\textsubscript{1.1}Zn\textsubscript{11} and Co\textsubscript{2}Pd\textsubscript{2}Zn\textsubscript{8} single phases in Co–Pd–Zn system, amongst them, the studied magnetic properties of the Co\textsubscript{2}Pd\textsubscript{2}Zn\textsubscript{8} phase exhibit ferromagnetism mainly due to Co atoms. If we carefully look into the local structure of the compound, Co and Pd atoms are randomly distributed in OT and OH sites of a 26-atom \(\gamma\)-brass cluster.\(^{13}\) Hence, the magnetic exchange interaction is reasonably strong between Co atoms located at OT and OH sites within bonding interaction (Co–Co \(\approx 2.73\) Å) to show long-range magnetic ordering (i.e. ferromagnetism). Compared to our system in Co\textsubscript{2–x}Ni\textsubscript{x}Zn\textsubscript{11}, where Co and Ni atoms are statistically distributed at OT sites of a 26-atom \(\gamma\)-brass cluster. The system pos-
sesses two kinds of interaction (say, 4.36 Å and 4.90 Å) of homonuclear atoms (Co–Co and Ni–Ni). Keeping in mind the orbital contribution of the respective atom at the Fermi level (\(E_F\)) for the corresponding compositions, the Co–Co varies from four to two to zero per unit cell for Co\(_{1.5}\)Ni\(_{0.5}\)Zn\(_{11}\), Co\(_{1.0}\)Ni\(_{1.0}\)Zn\(_{11}\), and Co\(_{0.5}\)Ni\(_{1.5}\)Zn\(_{11}\), respectively (Fig. 12). In opposite, the Ni–Ni interaction is more significant for the Co\(_{0.5}\)Ni\(_{1.5}\)Zn\(_{11}\) as shown in Fig. 13. It should affect the magnetic exchange interaction between Co or Ni atoms since \(I\) (magnetic exchange interaction) strongly related to the local structure of the individual magnetic elements. This interaction distance is out of bonding treatment, so it is supposed to fail the long-range magnetic ordering due to the weak magnetic exchange interaction between Co or Ni atoms.

4. Summary

Pseudo-binary \(\gamma\)-brass type phases Co\(_{2-x}\)Ni\(_x\)Zn\(_{11}\) \((x = 0.3-1.8)\) were prepared by a high-temperature conventional synthetic route. This pseudo-binary phase adopts a \(\gamma\)-brass structure type \((I4/m\ 22\ 7\), \(a \approx 9\ \text{Å})\). The structure consists of 26-atom clusters of four nested polyhedra arranged in bcc packing. A 26-atom cluster is constructed from an inner tetrahedron (IT), an outer tetrahedron (OT), an octahedron (OH), and a distorted cuboctahedron (CO). The preliminary model built based on SCXRD and EDS data analyses suggests that in the 26-atom cluster, IT, OH, and CO sites are completely occupied by Zn atoms and the OT sites show statistical mixing of Co and Ni in the Co\(_{2-x}\)Ni\(_x\)Zn\(_{11}\), which is further confirmed by NPD data refinements. As the Ni content increases, the site occupancy of Ni at the OT site increases in Co\(_{2-x}\)Ni\(_x\)Zn\(_{11}\). Theoretical electronic structure calculations point out that the ‘OT model’ is the lowest energy model amongst the four considered models (IT model, OT model, OH model, and CO model), where Ni atoms substitute Co at OT sites in the structure of Co\(_{2-x}\)Ni\(_x\)Zn\(_{11}\) \((x = 0.3-1.8)\). The DOS curve for Co\(_{1.5}\)Ni\(_{0.5}\)Zn\(_{11}\) discerns a similar feature as binary Co\(_2\)Zn\(_{11}\). The wide pseudo-gap is formed near \(E_F\) in the compositions of Co\(_{1.0}\)Ni\(_{1.0}\)Zn\(_{11}\) and Co\(_{0.5}\)Ni\(_{1.5}\)Zn\(_{11}\), since OT (Ni/Co)-IT/OH/CO (Zn) contacts get optimized as Ni-concentration is increased. Conversely, the homo-atomic Zn–Zn contacts give \(\sim\)60% to the stability of the compound as found from bonding analysis. Magnetic properties of Co\(_{2-x}\)Ni\(_x\)Zn\(_{11}\) are rationalized from the features of the two binary end compositions, Co\(_2\)Zn\(_{11}\) and Ni\(_2\)Zn\(_{11}\). The magnetic measurements of the three samples indicate that there is a change in magnetic property from paramagnetic to diamagnetic as the Ni content gradually increases in the

\[\text{Fig. 12} \quad \text{The variation of the local environment of Co atoms within the unit cell: Co}_{1.5}\text{Ni}_{0.5}\text{Zn}_{11} \text{ (left), Co}_{1.0}\text{Ni}_{1.0}\text{Zn}_{11} \text{ (middle), and Co}_{0.5}\text{Ni}_{1.5}\text{Zn}_{11} \text{ (right).}\]

\[\text{Fig. 13} \quad \text{The variation of the local environment of Ni atoms within the unit cell: Co}_{1.5}\text{Ni}_{0.5}\text{Zn}_{11} \text{ (left), Co}_{1.0}\text{Ni}_{1.0}\text{Zn}_{11} \text{ (middle), and Co}_{0.5}\text{Ni}_{1.5}\text{Zn}_{11} \text{ (right).}\]
pseudo-binary Co$_{2-x}$Ni$_x$Zn$_{11}$. In agreement with the magnetic property measurement, NPD data showed no evidence of long-range magnetic ordering in the system.

**Author contributions**


**Data availability**

The data supporting this article have been included as part of the ESL. Crystallographic data for (SC1, SC2, SC3, and SC4) have been deposited at the CCDC under [CCDC 230799, 2307993, 2307992, and 2307994†].

**Conflicts of interest**

I, on behalf of the co-authors, declare that we have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**References**