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Atomic Distributions in the γ-Brass Structure of the Cu–Zn System: A Structural and Theoretical Study

Abstract
The crystal structures, atomic distributions, and theoretical electronic structures of five different Cu$_{5-x}$Zn$_{8+x}$ γ-brass compounds ($x = -0.59(3)$, $-0.31(3)$, $0.00(3)$, $0.44(3)$, and $0.79(3)$) are reported with the goal of identifying chemical influences on the observed phase width. These structures have been refined by both neutron and X-ray powder diffraction to obtain accurate crystal chemical parameters. All compounds crystallize in the space group $I43m$ (No. 217) ($Z = 4$), and the unit cell parameters are $a = 8.8565(4)$, $8.8612(5)$, $8.8664(3)$, $8.8745(4)$, and $8.8829(7)$ Å, respectively, for Cu$_{5.59}$Zn$_{7.41}$, Cu$_{5.31}$Zn$_{7.69}$, Cu$_{5.00}$Zn$_{8.00}$, Cu$_{4.56}$Zn$_{8.44}$, and Cu$_{4.21}$Zn$_{8.79}$. The results indicate specific site substitutions on both sides of the ideal composition “Cu$_5$Zn$_8$”. In all cases, the 26-atom cluster building up the γ-brass structure shows a constant inner [Cu$_4$Zn$_4$] tetrahedral star with compositional variation occurring at the outer octahedron and cuboctahedron. First principles and semiempirical electronic structure calculations using both a COHP and Mulliken population analysis were performed to understand the observed compositional range and to address the “coloring problem” for the site preferences of Cu and Zn atoms for this series of compounds.

Disciplines
Materials Chemistry | Other Chemistry | Physical Chemistry

Comments

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Atomic Distributions in the $\gamma$-Brass Structure of the Cu–Zn System: A Structural and Theoretical Study

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The crystal structures, atomic distributions, and theoretical electronic structures of five different Cu$_{5-x}$Zn$_{8+x}$ $\gamma$-brass compounds ($x = -0.59(3)$, $-0.31(3)$, $0.00(3)$, $0.44(3)$, and $0.79(3)$) are reported with the goal of identifying chemical influences on the observed phase width. These structures have been refined by both neutron and X-ray powder diffraction to obtain accurate crystal chemical parameters. All compounds crystallize in the space group $I4_1/amd$ (No. 129) ($Z = 4$), and the unit cell parameters are $a = 8.8565(4)$, $8.8612(5)$, $8.8664(3)$, $8.8745(4)$, and $8.8829(7)$ Å, respectively, for Cu$_{5.59}$Zn$_{7.41}$, Cu$_{5.31}$Zn$_{7.69}$, Cu$_{5.00}$Zn$_{8.00}$, Cu$_{4.56}$Zn$_{8.44}$, and Cu$_{4.21}$Zn$_{8.79}$. The results indicate specific site substitutions on both sides of the ideal composition “Cu$_5$Zn$_8$”. In all cases, the 26-atom cluster building up the $\gamma$-brass structure shows a constant inner [Cu$_4$Zn$_4$] tetrahedral star with compositional variation occurring at the outer octahedron and cuboctahedron. First principles and semiempirical electronic structure calculations using both a COHP and Mulliken population analysis were performed to understand the observed compositional range and to address the “coloring problem” for the site preferences of Cu and Zn atoms for this series of compounds.

Introduction

Reinvestigation of the Cu–Zn binary system in the $\gamma$-brass region, i.e., between 57 and 68 atom % Zn, is motivated by the relationship between the cubic $\gamma$-brass structure and various quasi-crystal approximants.1–10 $\gamma$-Brasses are included among Hume–Rothery electron phases, which achieve their stability by the interaction between the Fermi surface (a sphere with radius $k_F$ in reciprocal space in the free electron model) and the Brillouin zone (the convex polyhedra with faces located at planes perpendicular to $k/2$, where $k$ = a reciprocal lattice vector).11,12 According to Hume–Rothery’s principles of electron compounds,13,14 the cubic

![Figure 1. Representation of the Cu–Zn binary phase diagram in the range 30–80 atom % Zn and between 773 and 1273 K. Composition limits for the $\beta$ and $\gamma$ brasses are noted, as well as the Cu$_{5}$Zn$_{8}$ composition.](image-url)

γ′-brass phase is preferred for a valence electron concentration (vec = number of valence s and p electrons/number of atoms in the chemical formula) of 1.61 = 21/13 s and p electrons/atom. In the Cu–Zn binary system, this concept leads to the “ideal” composition of “Cu5Zn4”, i.e., 61.5 atom % Zn. However, a wide range of composition has been observed around both sides of this concentration, although no detailed reports on the distribution of Cu and Zn among the various sites in the crystal structure exist.

Within the nearly free electron theory of electronic structure for metals, the composition range in Cu–Zn γ′-brasses is nicely explained by an argument presented by Jones and Mott.\(^\text{(15,16)}\) They constructed a large polyhedral zone, called a “Jones zone”, from the 36 (330) and (411) planes in reciprocal space, planes which give large structure factors for the γ′-brass structure and could show that the space enclosed accommodates 1.73 “free” valence electrons per atom.\(^\text{(17)}\) This zone is nearly spherical, and an inscribed sphere (i.e., a sphere just touching the polyhedral faces) holds 1.54 free valence electrons per atom.\(^\text{(18)}\) In this picture, the valence d electrons are treated as tightly held by the nuclei and do not contribute to the free electrons; these are assigned to the valence s and p electrons. In the Mott and Jones model, the spherical Fermi surface will be distorted when it approaches the faces of the Jones zone, opening energy gaps in the band structure near these positions in reciprocal space and providing some energetic stabilization relative to other structures (i.e., other translational periodicities).

There remains, however, some controversy regarding the origin of the stability of the γ′-brass phases. Paxton et al. assign its stability to a lowering of the density of states around 1.7 electrons per atom.\(^\text{(19)}\) Furthermore, they assign gaps opening throughout the Brillouin zone as arising from scattering from (330), {411} as well as {420}, {332}, and {422} planes, while it is the distortion of the atomic planes with respect to the body-centered cubic (bcc) structure in real space that enhances the scattering from the {411}, especially, and {330} planes. Subsequently, Mizutani et al. have analyzed the free electron bands and argue that the (330) and {411} planes have the dominant role in creating a declining slope of the density of states curve at the Fermi level.\(^\text{(17,19–23)}\) Unfortunately, existing arguments based on the nearly free electron model and other related approaches of electronic structure for metals do not address the chemical structure of these intermetallics, that is, how the various atoms are arranged.\(^\text{(24–26)}\)

In this paper, we report the crystal structures of five different Cu\(_x\)Zn\(_{8-x}\) samples for \(x = -0.59(3), -0.31(3), 0.00(3), 0.44(3),\) and 0.79(3) with the cubic γ′-brass structure, as refined by both neutron and X-ray powder diffraction. This range corresponds to the existence of the γ′-brass structure (57–68 atom % Zn) in the Cu–Zn phase diagram, shown in Figure 1. Our crystallographic work focuses on the “coloring problem”\(^\text{(29)}\) of Cu and Zn atoms among the different crystallographic sites. Given the similar X-ray scattering factors for Cu and Zn, a combination of X-ray and neutron diffraction is necessary to obtain accurate structural chemical information in these Cu–Zn phases. X-ray and neutron diffraction studies of Cu–Al and Cu–Al–Zn γ′-brasses have already been successful at distinguishing site occupancy patterns and structural distortions over the observed composition range.\(^\text{(30,31)}\) The factors influencing one atomic arrangement over another in a solid-state structure are defined by energetic contributions originating from the site potentials and pairwise interatomic potentials. These are, respectively, the site energy and the bond energy, which can be assessed by a population analysis of the calculated electronic structure.\(^\text{(29)}\) Within the tight-binding approximation, the band energy can be decomposed into

\(Gourdon\ et\ al.\)

\(\text{Table 1. Compositions, Unit Cell Parameters, Refined Compositions, and Refinement Statistics for Cu}_{x}\text{-Zn}_{8-x}\ (x = -0.59, -0.31, 0.00, 0.44,\) and 0.79)

<table>
<thead>
<tr>
<th>loaded composition (%)</th>
<th>Cu(<em>{5.05})Zn(</em>{8.41})</th>
<th>Cu(<em>{5.04})Zn(</em>{8.40})</th>
<th>Cu(<em>{4.98})Zn(</em>{8.40})</th>
<th>Cu(<em>{4.98})Zn(</em>{8.41})</th>
<th>Cu(<em>{6.07})Zn(</em>{7.97})</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDX composition</td>
<td>(Cu(<em>{0.78})Zn(</em>{0.57}))</td>
<td>(Cu(<em>{0.78})Zn(</em>{0.57}))</td>
<td>(Cu(<em>{0.78})Zn(</em>{0.57}))</td>
<td>(Cu(<em>{0.78})Zn(</em>{0.57}))</td>
<td>(Cu(<em>{0.78})Zn(</em>{0.57}))</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.8562(6)</td>
<td>8.8605(3)</td>
<td>8.8674(2)</td>
<td>8.8747(5)</td>
<td>8.8835(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>2.083</td>
<td>1.656</td>
<td>1.682</td>
<td>2.077</td>
<td>2.046</td>
</tr>
</tbody>
</table>

\(^\text{(22) Schubert, K. Z. Metallkd. 1989, 80, 783.}\)
\(^\text{(24) Bradley, A. J. Physicue 1949, 13, 170.}\)
the sum of site energy and bond energy terms according to eq 1

\[ E_{\text{Band}} = E_{\text{Site}} + E_{\text{Bond}} = \left( \sum_i q_i \alpha_{ij} \right)_{\text{Site}} + \left( \sum_{ij} p_{ij} \beta_{ij} \right)_{\text{Bond}} \]

(1)

where \( \alpha_{ij} \) and \( \beta_{ij} \) are coulomb and resonance integrals, \( q_i \) values are the orbital occupation numbers, and \( p_{ij} \) values are the overlap populations involving orbitals \( i \) and \( j \). To analyze these contributions in the Cu–Zn system and to identify the chemical parameters consistent with the specific ordering, tight-binding, linear muffin-tin orbital calculations within the atomic sphere approximation (TB-LMTO-ASA)\(^{(32)}\) have been carried out on the series Cu\(_5.59\)Zn\(_{7.41}\), Cu\(_5.31\)Zn\(_{7.69}\), Cu\(_5.00\)Zn\(_{8.00}\), Cu\(_4.56\)Zn\(_{8.44}\), and Cu\(_4.21\)Zn\(_{8.79}\). We also performed similar ab initio calculations on the \( \beta \)-brass CuZn phase in order to interpret the phase diagram boundaries between the \( \beta \) and \( \gamma \) phases. We believe this combination of structural and theoretical analysis provides some new insights into the behavior of these Hume–Rothery phases.

**Experimental Section**

**A. Synthesis and Chemical Analysis.** Five different Cu–Zn samples were targeted by combining the pure elements, copper (powder, Fisher, 99.999%) and zinc (powder, Fisher, 99.999%), in the Zn atomic percentages of 57.0, 59.0, 61.5, 65.0, and 67.5. The alloys were annealed at 1073 K in evacuated silica tubes for 2 days, then slowly cooled to 900 K, and finally quenched in water to prevent any formation of superstructure or long-range ordering at lower temperatures.\(^{(33,34)}\) Indeed, in the similar Zn–Pd system we recently observed that long-range ordered modulated structures in these \( \gamma \)-brass systems might be synthesized by slow cooling.\(^{(3,10)}\) The Cu–Zn samples are stable upon exposure to air and water. Electron microprobe analyses were performed using a JEOL JXA-8200 and with the pure elements as standards to obtain quantitative values. These analytical results are summarized in Table 1, which shows excellent agreement with both the loaded compositions and those refined from subsequent diffraction experiments.

**B. Crystal Structure Determination by Powder Diffraction.**

**B1. X-ray Diffraction:** X-ray powder diffraction patterns of these phases were recorded on a Rigaku Ultima III diffractometer mounted on a sealed tube generator with a Cu target, using \( \text{K}_{\alpha 1} \) and \( \text{K}_{\alpha 2} \) radiations. Data were collected at 0.02° steps for 5 s/step over the 2\( \theta \) range 5–90°. Figure 2a shows the observed and calculated patterns along with the difference curve for Cu\(_{4.21}\)Zn\(_{8.79}\). Figure 2b shows the five diffraction patterns in the 2\( \theta \) range 42–50° observed for Cu\(_{5.59}\)Zn\(_{7.41}\), Cu\(_{5.31}\)Zn\(_{7.69}\), Cu\(_{5.00}\)Zn\(_{8.00}\), Cu\(_{4.56}\)Zn\(_{8.44}\), and Cu\(_{4.21}\)Zn\(_{8.79}\). The slightly shifting diffraction peaks as the composition also illustrated on the same scale. (b) X-ray powder diffraction patterns in the 2\( \theta \) range 42–50° observed for Cu\(_{5.59}\)Zn\(_{7.41}\), Cu\(_{5.31}\)Zn\(_{7.69}\), Cu\(_{5.00}\)Zn\(_{8.00}\), Cu\(_{4.56}\)Zn\(_{8.44}\), and Cu\(_{4.21}\)Zn\(_{8.79}\).

**B2. Neutron Diffraction:** Since the scattering factors for Cu and Zn may not permit distinguishing these atoms by X-ray powder diffraction (just one electron difference), neutron powder diffraction was carried out on these compounds. Indeed, the elastic neutron cross sections for Cu (7.718 \( \times \) 10\(^{-22} \)) cm\(^2\) and Zn (5.680 \( \times \) 10\(^{-24} \)) cm\(^2\) are significantly different to allow us to refine site distributions. Time-of-flight (TOF) neutron diffraction data were collected at ambient conditions on the Neutron Powder Diffraction Center of Los Alamos National Laboratory. This instrument is a high-resolution powder diffractometer located at flight path 1, 32 m from the spallation neutron target. The data were collected at 295 K using the 148°, 119°, 90°, and 46° banks, which cover a d-spacing range from 0.12 to 7.2 Å. Figure 3 illustrates the observed and calculated neutron diffraction patterns for Cu\(_{4.21}\)Zn\(_{8.79}\) as an example.

The structure was refined using the General Structure Analysis System, a Rietveld profile analysis program developed by Larson and Von Dreele.\(^{(39)}\) The starting structural models for each composi-

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atomic positions, isotropic thermal displacement parameters, and composition and microprobe analyses. The unit cell parameters, chemical compositions are generally within 2 atom % of the loaded specific mixed Cu/Zn sites are listed in Table 2. The refined allowed the occupancies to be refined. After relaxation of the absorption were also refined for a total of 61 parameters. In order factors, isotropic strain terms in the profile function, and sample isotropic displacement parameters. Background coefficients, scale banks) for unit cell parameters, atomic positions, and equivalent displacement parameters. The difference curve is illustrated in blue on the same scale. These linear relationships corroborate the refined site occupations and resulting compositions and argue against vacancies in these structures according to our synthetic procedures.

The cubic γ-brass structure is a relatively complicated one having 52 atoms in the unit cell. Various descriptions have been proposed in the past. The most traditional one involves the 26-atom cluster constructed from successive polyhedral shells: (a) an inner tetrahedron of M2 atoms; (b) an outer tetrahedron of M1 atoms sitting above the faces of the inner tetrahedron; (c) an octahedron of M3 atoms lying above the edges of the outer tetrahedron; (d) a distorted cuboctahedron of M4 atoms placed above the edges of the octahedron (Figure 5). These polyhedra adopt a bcc packing; this structure, as pointed out in the introduction. Various descriptions have been proposed in the past. The most traditional one involves the 26-atom cluster constructed from successive polyhedral shells: (a) an inner tetrahedron of M2 atoms; (b) an outer tetrahedron of M1 atoms sitting above the faces of the inner tetrahedron; (c) an octahedron of M3 atoms lying above the edges of the outer tetrahedron; (d) a distorted cuboctahedron of M4 atoms placed above the edges of the octahedron (Figure 5). These polyhedra adopt a bcc packing; this structure, as pointed out in the introduction.
Another description of this structure involves the local environments at each of the four distinct crystallographic sites, which are illustrated in Figure 5 using a distance cutoff of 2.9 Å. The M1 and M2 sites are coordinated by distorted icosahedra, whereas the M3 and M4 sites show 13-atom and 11-atom coordination environments, respectively. Four M1 sites forming the outer tetrahedron in the 26-atom cluster and their coordinating icosahedra create another possible fundamental building block for the γ-brass structure: four interpenetrating M1-centered icosahedra, which can be formulated as $[\text{M1}(\text{M2}^{3/3}\text{M3}^{3/2}\text{M4}^{6/2})]^4$. A survey of the interatomic distances, listed in Table 3, indicates that the two icosahedral sites, M1 and M2, have shorter average distances to their coordinating atoms than those for the M3 and M4 sites. Likewise, the M1 and M2 have lower isotropic displacement parameters than the M3 and M4 sites (see Table 2). The relative complexity of the atomic structure and the presence of these icosahedra highlight the quasi-crystal approximant character of this phase.

For the ideal composition Cu$_5$Zn$_8$, the M1 and M3 sites are fully occupied by Cu atoms, whereas the M2 and M4 sites are fully occupied by Zn atoms; i.e., the 26-atom cluster is formulated as $[\text{Zn}_4\text{Cu}_4](\text{Cu})_{6}(\text{Zn})_{12}$. This distribution pattern leads to shorter (on average) heteronuclear Cu–Zn distances and longer homonuclear Cu–Cu and Zn–Zn distances in Cu$_5$Zn$_8$. As the chemical composition varies, our neutron diffraction results indicate that substitutions are restricted to either the M3 or M4 sites, with the specific tendency depending upon how the composition changes—there is no redistribution of Cu and Zn among the M3 and M4 sites. With respect to the 26-atom, “classical” γ-brass cluster, the inner and outer tetrahedra are completely occupied by Zn and Cu atoms, respectively, creating a [Zn$_4$Cu$_4$] tetrahedral star core; variations in composition occur

![Figure 5](image_url)

**Table 3.** Interatomic Distances in Cu$_{5+x}$Zn$_{8-x}$ ($x = -0.59$, $-0.31$, $0.00$, $0.44$, and $0.79$) As Determined from Neutron Powder Diffraction at 298 K

<table>
<thead>
<tr>
<th>Distance</th>
<th>Cu$<em>{5.59}$Zn$</em>{7.41}$</th>
<th>Cu$<em>{5.31}$Zn$</em>{7.69}$</th>
<th>Cu$<em>{5.00}$Zn$</em>{8.00}$</th>
<th>Cu$<em>{4.56}$Zn$</em>{8.44}$</th>
<th>Cu$<em>{4.21}$Zn$</em>{8.79}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1–M4</td>
<td>2.5440(8)</td>
<td>2.5466(7)</td>
<td>2.5810(9)</td>
<td>2.5445(8)</td>
<td>2.5947(9)</td>
</tr>
<tr>
<td>M4 (s)</td>
<td>2.5873(7)</td>
<td>2.5775(7)</td>
<td>2.6114(8)</td>
<td>2.5930(8)</td>
<td>2.6077(8)</td>
</tr>
<tr>
<td>M2 (s)</td>
<td>2.5604(8)</td>
<td>2.5607(7)</td>
<td>2.5810(9)</td>
<td>2.5704(8)</td>
<td>2.6061(8)</td>
</tr>
<tr>
<td>M3 (s)</td>
<td>2.7007(7)</td>
<td>2.7074(5)</td>
<td>2.7037(9)</td>
<td>2.7135(11)</td>
<td>2.6976(8)</td>
</tr>
<tr>
<td>average</td>
<td>2.6098(8)</td>
<td>2.6346(7)</td>
<td>2.6319(9)</td>
<td>2.6329(9)</td>
<td>2.6315(8)</td>
</tr>
<tr>
<td>M2–M3 (s)</td>
<td>2.5781(6)</td>
<td>2.5804(7)</td>
<td>2.5465(9)</td>
<td>2.5952(9)</td>
<td>2.5402(8)</td>
</tr>
<tr>
<td>M3 (s)</td>
<td>2.6074(8)</td>
<td>2.6207(7)</td>
<td>2.5881(8)</td>
<td>2.6034(7)</td>
<td>2.6155(8)</td>
</tr>
<tr>
<td>M4 (s)</td>
<td>2.6277(7)</td>
<td>2.6327(8)</td>
<td>2.6114(8)</td>
<td>2.6289(7)</td>
<td>2.6777(8)</td>
</tr>
<tr>
<td>M2 (s)</td>
<td>2.7046(8)</td>
<td>2.7048(8)</td>
<td>2.7043(7)</td>
<td>2.7129(7)</td>
<td>2.6792(8)</td>
</tr>
<tr>
<td>average</td>
<td>2.6294(8)</td>
<td>2.6131(7)</td>
<td>2.6126(8)</td>
<td>2.6148(9)</td>
<td>2.6156(8)</td>
</tr>
<tr>
<td>M3–M4 (s)</td>
<td>2.5444(6)</td>
<td>2.5417(6)</td>
<td>2.5774(8)</td>
<td>2.5328(10)</td>
<td>2.5423(13)</td>
</tr>
<tr>
<td>M5 (s)</td>
<td>2.5541(8)</td>
<td>2.5553(8)</td>
<td>2.5572(11)</td>
<td>2.5526(8)</td>
<td>2.5460(7)</td>
</tr>
<tr>
<td>M2 (s)</td>
<td>2.5781(8)</td>
<td>2.5804(7)</td>
<td>2.5810(9)</td>
<td>2.5952(11)</td>
<td>2.5947(9)</td>
</tr>
<tr>
<td>M4 (s)</td>
<td>2.7007(8)</td>
<td>2.7074(6)</td>
<td>2.7043(7)</td>
<td>2.7135(11)</td>
<td>2.7129(8)</td>
</tr>
<tr>
<td>M3 (s)</td>
<td>2.8063(4)</td>
<td>2.8102(6)</td>
<td>2.8091(6)</td>
<td>2.8086(6)</td>
<td>2.8062(7)</td>
</tr>
<tr>
<td>average</td>
<td>2.7022(8)</td>
<td>2.7042(6)</td>
<td>2.7045(8)</td>
<td>2.7083(9)</td>
<td>2.7095(9)</td>
</tr>
<tr>
<td>M4–M3 (s)</td>
<td>2.5440(8)</td>
<td>2.5417(7)</td>
<td>2.5465(9)</td>
<td>2.5942(9)</td>
<td>2.5402(8)</td>
</tr>
<tr>
<td>M5 (s)</td>
<td>2.5541(8)</td>
<td>2.5553(8)</td>
<td>2.5572(11)</td>
<td>2.5526(8)</td>
<td>2.5460(7)</td>
</tr>
<tr>
<td>M2 (s)</td>
<td>2.5781(8)</td>
<td>2.5804(7)</td>
<td>2.5810(9)</td>
<td>2.5952(11)</td>
<td>2.5947(9)</td>
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<tr>
<td>M4 (s)</td>
<td>2.7007(8)</td>
<td>2.7074(6)</td>
<td>2.7043(7)</td>
<td>2.7135(11)</td>
<td>2.7129(8)</td>
</tr>
<tr>
<td>M3 (s)</td>
<td>2.8063(4)</td>
<td>2.8102(6)</td>
<td>2.8091(6)</td>
<td>2.8086(6)</td>
<td>2.8062(7)</td>
</tr>
<tr>
<td>average</td>
<td>2.7022(8)</td>
<td>2.7042(6)</td>
<td>2.7045(8)</td>
<td>2.7083(9)</td>
<td>2.7095(9)</td>
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<tr>
<td>M4–M3 (s)</td>
<td>2.5440(8)</td>
<td>2.5417(7)</td>
<td>2.5465(9)</td>
<td>2.5942(9)</td>
<td>2.5402(8)</td>
</tr>
</tbody>
</table>

at the outer regions of this cluster, i.e., the M3 and M4 sites, exclusively. The 26-atom cluster can be formulated as \{[\text{Zn}_4\text{Cu}_4](\text{M}3)_6(\text{M}4)_{12}\}. Relative to \text{Cu}_9\text{Zn}_6, \text{Cu}-rich species give \{[\text{Zn}_6\text{Cu}_4](\text{Cu}_9\text{Zn}_{1-a})_{12}\} and \text{Zn}-rich species give \{[\text{Zn}_4\text{Cu}_6](\text{Cu}_{1-b}\text{Zn}_6)(\text{Zn})_{12}\}. Closer examination of the interatomic distances associated with the M1 and M2 sites reveals an interesting relationship between atomic distributions and distances: in the \text{Cu}-rich species (\text{Cu}_{5.6}\text{Zn}_{8.6}), \text{Cu} substitutes at the M4 sites, which have the shortest distances to the M1 (Cu) sites and the longest distances to the M2 (Zn) sites; in the \text{Zn}-rich species (\text{Cu}_{5.3}\text{Zn}_{8.4}), \text{Zn} substitutes at the M3 sites, which have the longest distances to the M1 (Cu) sites and the shortest distances to the M2 (Zn) sites.

Electronic Structure Calculations

To understand the relative stability of the \(\gamma\)-brass phase from a chemical perspective as well as the specific site substitution patterns for \text{Cu} and \text{Zn} and composition range in \text{Cu}_{5-x}\text{Zn}_{x+1}, electronic structure calculations have been carried out on various \(\gamma\)-brass and \(\beta\)-brass models in the \text{Cu}\text{--Zn} system with TB-LMTO-ASA\(^{42}\) using the LMTO, version 4.7, program.\(^{41}\) In this approach, exchange and correlation were treated in a local density approximation.\(^{42}\) All relativistic effects except spin–orbit coupling were taken into account using a scalar relativistic approximation.\(^{43}\) The radii of the Wigner–Seitz (WS) spheres were obtained by requiring the overlapping potential to be the best possible approximation to the full potential according to an automatic procedure; no empty spheres were necessary.\(^{44}\) The WS radii determined by this procedure were 1.42 Å for \text{Cu} and 1.53 Å for \text{Zn}. The basis sets included 4s, 4p, and 3d orbitals for \text{Cu} and \text{Zn}. The \(\mathbf{k}\)-space integrations to determine self-consistent charge densities, densities of states (DOS), and crystal orbital Hamilton populations (COHP)\(^{45}\) were performed by an improved tetrahedron method\(^{46}\) on grids of 400–600 \(\mathbf{k}\)-points of the corresponding irreducible wedges of the first Brillouin zones.

\(\gamma\)-Cu\(_{5-x}\)Zn\(_{x+1}\): Figure 6 illustrates the energy bands and the DOS and COHP curves for \text{Cu}\text{--Zn}, \text{Cu}\text{--Cu}, and \text{Zn}\text{--Zn} interatomic contacts of \text{Cu}_9\text{Zn}_6 in a 14 eV energy window surrounding the Fermi level. The partial DOS curves of the \text{Cu} and \text{Zn} contributions are represented in red and blue, respectively. The 4s and 4p orbitals of \text{Cu} and \text{Zn} form broad, nearly free electron-like energy bands. A large peak around 7.5 eV below the Fermi level mainly arises from \text{Zn} 3d states overlapping with \text{Cu} 4p wavefunctions, whereas between 2.5 and 4 eV below the Fermi level, a broader peak is identified to be mostly \text{Cu} 3d states overlapping with \text{Zn} valence 4p orbitals. Between 0.5 eV below and above the Fermi level, the DOS curve shows a significant reduction in value, i.e., a pseudogap that is primarily caused by d–p hybridization. Assuming a rigid-band approximation, we have located the Fermi levels for \text{Cu}_{5.59}\text{Zn}_{7.41} (150.4 eV; \text{vec} = 1.570, 57.0 atom % \text{Zn}) and \text{Cu}_{4.21}\text{Zn}_{8.79} (151.8 eV; \text{vec} = 1.676; 67.6 atom % \text{Zn}) on this DOS curve by the gray window. These boundaries correspond very well with the limits of the pseudogap and also identify the upper and lower limits for the existence of the \(\gamma\)-brass structure in the \text{Cu}\text{--Zn} diagram (see Figures 1 and 4).

(41) Krier, G.; Jepsen, O.; Burkhart, A.; Andersen, O. K. Tight-Binding LMTO, version 4.7; Max-Planck-Institut für Festkörperforschung: Stuttgart, Germany, 1997.
Distributions in the γ-Brass Structure of the Cu–Zn System

Table 4. Various Atomic Arrangements for Cu₅Zn₈ within the Cubic γ-Brass Structure and Their Relative Total Energies per Atom (eV)

<table>
<thead>
<tr>
<th>Space group</th>
<th>M₁ (M'₁)</th>
<th>M₂ (M'₂)</th>
<th>M₃ (M'₃)</th>
<th>M₄ (M'₄)</th>
<th>Formula</th>
<th>Energy/atom (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>P₄/mmm</td>
<td>Cu</td>
<td>Zn</td>
<td>Cu</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
<tr>
<td>B</td>
<td>P₄/mmm</td>
<td>Zn</td>
<td>Cu</td>
<td>Cu</td>
<td>Zn</td>
<td>Zn(Zn₂Cu₄)</td>
</tr>
<tr>
<td>C</td>
<td>P₄/mmm</td>
<td>Zn</td>
<td>Cu</td>
<td>Zn</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
<tr>
<td>D</td>
<td>P₄/mmm</td>
<td>Cu</td>
<td>Cu</td>
<td>Zn</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
<tr>
<td>E</td>
<td>P₄/mmm</td>
<td>Zn</td>
<td>Zn</td>
<td>Zn</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
<tr>
<td>F</td>
<td>P₄/mmm</td>
<td>Zn</td>
<td>Zn</td>
<td>Zn</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
<tr>
<td>G</td>
<td>P₄/mmm</td>
<td>Zn</td>
<td>Cu</td>
<td>Zn</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
<tr>
<td>H</td>
<td>P₄/mmm</td>
<td>Zn</td>
<td>Zn</td>
<td>Zn</td>
<td>Zn</td>
<td>Cu(Zn₂Cu₄)</td>
</tr>
</tbody>
</table>

* Models adopting the P₄/mmm space group have two inequivalent sets of sites.

In the energy band structure, significant band gaps across the Fermi level for Cu₅Zn₈ are mostly seen at the high symmetry points N (1/2, 1/2, 0) and Γ (0, 0, 0). In the Pd–Zn system, we have observed the existence of lattice modulations along the [110] directions, which suggests that the fraction of occupied states along the ΓN direction in the Brillouin zone significantly influences the observed γ-brass structures. Furthermore, the upper bound of the pseudogap corresponds to the bottom of parabolic ("free-electron-like") bands at points N and H (1/2, −1/2, 1/2). The Cu–Zn COHP curve identifies the upper bound point as the energy (Fermi level) that optimizes heteroatomic pairwise interactions; this energy corresponds to 151.8 valence s, p, and d e⁻ per formula unit, i.e., Cu₄₂Zn₈. While the heteroatomic interactions are optimized at this electron count, both the Cu–Zn, Cu–Zn, and Zn–Zn interactions remain weakly bonded. Therefore, increasing substitution of Cu by Zn in Cu₅–Zn₈ will eventually populate Cu–Zn antibonding states first in the γ-brass structure and lead to structural instability. Regarding the lower limit (Cu-rich side), the argument is less clear, although we observe that the Cu–Zn and Zn–Zn interactions are strongly bonding at ca. 0.7 eV below the Fermi level. Depopulating these bonding states by continuing to increase the Cu concentration will also lead to structural instability. Thus, the range of the pseudogap in the DOS for Cu₅–Zn₈ can be attributed to significant changes in pairwise orbital interactions.

Before considering various substitution patterns on the γ-brass structure, we address the distribution of Cu and Zn atoms in stoichiometric Cu₅Zn₈. TB-LMTO-ASA calculations on various distributions within the cubic cell, listed in Table 4, give the lowest energy arrangement (A) in exact agreement with structural characterizations: Cu in M₁ and M₃ sites, Zn in M₂ and M₄ sites, space group P₄/mmm. The highest energy configuration is also bcc but with Cu and Zn atoms switching the inner and outer tetrahedron sites, M₁ and M₂ (B). Another low-energy configuration (F) is a primitive cubic arrangement that maintains [Zn₄Cu₄] tetrahedral stars at the corners and center of the unit cell but modifies the distribution of Cu and Zn atoms at the M₃ and M₄ sites. The integrated COHP values for all pairwise interactions less than 2.90 Å indicate that the high energy arrangement B creates significant repulsive (antibonding) Zn–Zn interactions between the M₁ and M₄ sites, the distances of which are two of the shortest in the entire structure. In the observed arrangement A, these M₁–M₄ contacts are Cu–Zn and attractive (net bonding). Thus, there is an important bond energy contribution to the "coloring" of the γ-brass structure.

On the other hand, the TB-LMTO-ASA method is not well-suited to address the site energy contribution due to the tails of the wavefunctions that contribute to integrated "charges" within each WS sphere. We can analyze the significance of this term, however, by utilizing semiempirical, extended Hückel theory (EHT) to calculate relative atomic Mulliken populations. Relative atomic Mulliken populations for each crystallographic site in a structure (⟨Q⟩ − ⟨Q⟩₀) are evaluated by setting the atomic orbital parameters to be the same for every site in the crystal structure and calculating the difference between the calculated site population at each site (Q₀) and the average value overall sites ⟨⟨Q⟩⟩ for a range of valence electron counts. In this way, when the relative atomic Mulliken population at a site is negative, then the site is attractive for greater than average valence electron density; when it is positive, then the site is attractive for lower than average valence electron density. For this calculation on the Cu–Zn γ-brass structure, we do not include the valence 3d atomic orbitals on Cu or Zn because both are formally filled as seen in the DOS curve in Figure 6 but, rather, utilize just the 4s and 4p atomic orbitals, which are expressed as single-ζ Slater-type orbitals in EHT. Including the valence 3d orbitals changes the quantitative but not the qualitative results of the calculations. Diagonal Hamiltonian matrix elements are given by valence state orbital energies derived from atomic spectra for Zn; off-diagonal Hamiltonian matrix elements are approximated by the weighted Wolfberg–Helmholz approximation. The atomic parameters are as follows: Zn 4s, Hₐₙ = −12.41 eV, z₁ = 2.01; Zn 4p, Hₐₙ = −6.53 eV, z₁ = 1.70. With the use of the monatomic model, the relative Mulliken populations for the four crystallographic sites are plotted in Figure 7 as a function of vac; such plots were valuable for predicting site preferences for Mg, Zn, and Al in quasi-crystal approximant Bergmann phases. For the range of observed γ-brass structures, the M₂ and M₄ sites clearly attract the greater valence electron density, while the M₁ and M₃ sites attract the lower valence electron density. Within the approximation of filled 3d orbitals at both Cu and Zn for these intermetallics, Zn has greater valence electron density than Cu, such that

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Zn would be preferentially attracted to the M2 and M4 sites and Cu to the M1 and M3 sites. In earlier applications of the relative Mulliken populations, the electronegativities of the atomic constituents were used as a guide but do not work for the Cu–Zn system: Cu is more electronegative than Zn,55 which can be attributed to the filled 3d levels of Zn not found in Cu. However, the 4s orbital energy of Zn is lower than that of Cu. Thus, there are both site energy and bond energy factors contributing to the observed distribution of Cu and Zn in the observed γ-brass phases.

γ-Cu₁₂₃Zn₈₇₉₅ (Zn-Rich Cases): From the atomic arrangement in stoichiometric Cu₂Zn₈, Zn can replace Cu at either the M1 or M3 sites. To understand the site preference for the additional Zn, the total energies of six different models of a hypothetical “Cu₁₂₃Zn₆₅” (“CuZn₈” as an approximation to Cu₁₂₃Zn₈₇₉₅) compound were calculated. To conduct this study, all calculations were performed in the space group \( P22_2 \), a subgroup of \( I43m \), and the WS radii for Cu and Zn were kept constant. Scheme 1 shows the correlation between the various Wyckoff sites of the space groups \( I43m \) and \( P22_2 \). Table 5 lists the different models of “Cu₁₂₃Zn₈₅” by identifying the sites occupied by the additional Zn atoms.

Table 5. Site Occupation Patterns and Relative Total Energies for Substitutions on Cu₂Zn₈

<table>
<thead>
<tr>
<th>models</th>
<th>Cu₁</th>
<th>Cu₂</th>
<th>Cu₃</th>
<th>Cu₄</th>
<th>Cu₅</th>
<th>Cu₆</th>
<th>Cu₇</th>
<th>Zn₁</th>
<th>Zn₂</th>
<th>Zn₃</th>
<th>Zn₄</th>
<th>Zn₅</th>
<th>Zn₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(\Delta V)</td>
<td>0</td>
<td>-0.26</td>
<td>-0.027</td>
<td>-0.045</td>
<td>-0.027</td>
<td>-0.026</td>
<td>-0.141</td>
<td>-0.141</td>
<td>-0.216</td>
<td>-0.141</td>
<td>-0.216</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Zn fully occupies all M2 and M4 sites). Notice that our study is not exhaustive of all the possible cases but is just representative. According to the relative total energies, the additional Zn atoms definitely prefer to occupy the M3 (12e) sites in the cubic structure, which agrees with our neutron diffraction experiments.

The shapes of the calculated DOS curves for the various models (not presented here) are quite similar to the one in Figure 6, so the factors distinguishing the different models are quite subtle. The major justification of the observed site preference is to strengthen the Cu–Zn and Zn–Zn interactions by occupying additional bonding states. Cu–Cu interactions also become more attractive, but the best model, Zn4, minimizes the number of nearest neighbor Cu–Cu contacts while maximizing the number of Cu–Zn interactions. The Zn–Zn contacts become less repulsive; the filled Zn 3d band creates a net antibonding Zn–Zn interaction, as indicated by its integrated COHP value. Previous studies on factors influencing metal atom distributions in polar intermetallic compounds indicate that heterometallic interactions are favored over homometallic ones, especially when electronegative metals like Ni, Zn, or Au are involved,53,54,56–58 because these elements tend to develop filled valence d and s bands. The site energy also influences the substitution pattern; the relative Mulliken populations for the M1 and M3 sites suggest that the M3 site is the better alternative for Zn, as this site attracts a lower electron density.

γ-Cu₁₅₉₅Zn₇₄₁ (Cu-Rich Cases): In a similar fashion, we have calculated the total energy of seven models of hypothetical “Cu₁₂₃Zn₂₈” to explore the site preferences for replacing Zn atoms with Cu. These results are also listed in Table 5, and the preferred M4 sites show a larger relative stability than we observed for the Zn-rich cases. The observed substitution pattern also serves to maximize the number of heteroatomic Cu–Zn contacts and lowers the number of Zn–Zn contacts. Although the COHP value for the Zn–Zn interactions is bonding near the Fermi level, it is net antibonding due to the filled 3d orbitals. Furthermore, the pattern maximizes the number of Cu–Cu contacts. The COHP curves for Cu–Cu and Zn–Zn contacts indicates that lowering the Fermi level by Cu substitution will make the Cu–Cu and Zn–Zn interactions less bonded (more repulsive in the case of Zn–Zn; less attractive for Cu–Cu).


The γ-brass phase is closely related to the β-brass phase, which corresponds to a bcc structural arrangement with randomly distributed Cu and Zn atoms. Indeed, we can generate the γ-brass arrangement of atoms by starting from a $3 \times 3 \times 3$ superstructure of this β-brass bcc packing of atoms followed by removing 2 atoms from the resulting 54-atom supercell (one from the corner, one from the center of the supercell) and then shifting the remaining atomic sites to the resulting coordinates (see Figure 8). However, this construction involves only the positions of atoms and does not address the distribution of elements: the β-brass phase is completely disordered whereas the γ-brass phase typically shows ordering among different crystallographic sites. In addition, Paxton et al. have shown that from an electronic structure perspective there is no basis for this description. It is, perhaps, important to note here that the cubic γ-brass structure remains unknown for any monatomic system (pure element), although there is a recent report of a Li$_{26}$ cluster found in a Li–Na–Ba phase that corresponds to the cluster building up the γ-brass structure.

The nearly free electron model accounts quite well for the observed compositions and vec ranges of the bcc-type β-brass structure and the complex cubic γ-brass structure in Hume-Rothery alloys. The tight-binding model, which offers some chemical interpretations, is also successful in sorting related structures and the coloring of Cu and Zn through the structure itself and the atomic arrangement enhances the gap and through interatomic interactions provides a justification for the atomic distribution.

To further explore the relationship between the bcc-type β-brass with the γ-brass structures, the relative total energies of various Cu$_{1-x}$Zn$_x$ models were evaluated via a tight-binding approach (TB-LMTO-ASA) and compared. Four different cases were probed: (1) β-brass (bcc-type); (2) γ-brass (52–atom cubic unit cell over 4 crystallographically distinct sites); (3) $2 \times 2 \times 2$ superstructure of the bcc arrangement with vacancies at the corners and center of the cell (14 atoms); and (4) $3 \times 3 \times 3$ superstructure of the bcc arrangement, also with vacancies at the corners and center of the cell (52 atoms). Models 1, 2, and 4 are depicted in Figure 8; model 3 represents an intermediate periodicity between the two observed structural motifs. To account for changes in vec and atomic volumes, the average atomic volumes were modified to reflect the experimental results, whereas the WS radii for Cu and Zn remained constant. Figure 10 illustrates the relative total energies of these models for compositions between 100% Cu to 100% Zn relative to the total energies of the compositionally weighted average from the hypothetical monatomic γ-brasses, “Cu$_{13}$” and “Zn$_{13}$”. This choice of reference specifically probes the bcc-related structures and the coloring of Cu and Zn through-
out the structures. We have not included the face-centered cubic and hexagonal close-packed (hcp) type structures for comparison.

The agreement with experiment is exceptionally good. These results reiterate the importance of the distortion from a defect-bcc packing of atoms toward stabilizing the γ-brass structure, and the enhancement occurs near 61.5 atom % Zn (vec = 1.615 valence electrons per atom). The 2 × 2 × 2 superstructure was selected for study because there does not seem to be any reason to exclude its existence from the (nearly) free electron model. In fact, using the free electron model to calculate the vec values associated with the first Brillouin zone and the Fermi sphere for this superstructure, we find a lower limit of 1.693 electrons per atom (Fermi sphere) and an upper limit of 2.286 electrons per atom, which lies higher than either the β-brass (1.481—2.000 electrons per atom) or the γ-brass (1.538—1.732 electrons per atom) structures. According to Figure 10, the 2 × 2 × 2 superstructure is energetically competitive near the transition between β- and γ-brasses and then is the preferred structure among these for vec values above ca. 1.75 (this is the range where hcp structures predominate). For all compositions, the 3 × 3 × 3 superstructure never becomes a competitive arrangement. Thus, this tight-binding approach provides an excellent separation of the two brass-type structures and also distinguishes them from reasonable bcc-related models.

**Summary**

Structural characterization of a series of Cu$_{5-x}$Zn$_x$ compounds (x = −0.59, −0.31, 0.00, 0.44, and 0.79) with the γ-brass structure shows a specific site distribution pattern around the ideal composition of Cu$_5$Zn$_8$. Of the four crystallographic sites, the two that are surrounded by an icosahedral environment and that form [Zn$_4$Cu$_4$] tetrahedral stars around the corners and centers of the unit cell refuse chemical substitution for the observed compositional range. This particular substitution pattern has been investigated by electronic structure calculations. These calculations identify influences from both site energies and bond energies on the observed coloring of this structure over the entire compositional range.

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**Supporting Information Available:** Neutron crystallographic files in CIF format for the structure determination of Cu$_{5.59}$Zn$_{7.41}$, Cu$_{5.31}$Zn$_{7.69}$, Cu$_{5.00}$Zn$_{8.00}$, Cu$_{4.56}$Zn$_{8.44}$, and Cu$_{4.21}$Zn$_{8.79}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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