

High-Pressure Synthesis

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Discovery of a Superconducting Cu–Bi Intermetallic Compound by High-Pressure Synthesis

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Abstract: A new intermetallic compound, the first to be structurally identified in the Cu–Bi binary system, is reported. This compound is accessed by high-pressure reaction of the elements. Its detailed characterization, physical property measurements, and *ab initio* calculations are described. The commensurate crystal structure of $\text{Cu}_{11}\text{Bi}_7$ is a unique variation of the NiAs structure type. Temperature-dependent electrical resistivity and heat capacity measurements reveal a bulk superconducting transition at $T_c = 1.36$ K. Density functional theory calculations further demonstrate that $\text{Cu}_{11}\text{Bi}_7$ can be stabilized (relative to decomposition into the elements) at high pressure and temperature. These results highlight the ability of high-pressure syntheses to allow for inroads into heretofore-undiscovered intermetallic systems for which no thermodynamically stable binaries are known.

The landscape of metastable compounds offers tremendous opportunity for the synthesis of new materials with unusual properties. In the simplest case, there are a large number of binary systems in which no structurally defined, or intermetallic, compounds are known. The absence of known binaries originates from wide miscibility gaps between the constituent elements that persist even at elevated temperatures, rendering these intermetallics metastable at ambient conditions. Isolation of these metastable compounds offers the potential for the realization of exotic properties, yet such species are inaccessible by traditional solid-state syntheses, which result in phase separation of the elements upon cooling. Consequently, there exist large regions of unexplored synthetic phase space and a dearth of knowledge on the chemical and physical properties in numerous binary systems.

Various non-conventional approaches, such as flux synthesis,^[1] topochemical pseudomorphosis,^[2] nanoparticle synthesis,^[3] and high-pressure synthesis,^[4] have emerged as methods for targeting these inherently metastable intermetallic phases. Employing these nontraditional techniques allows for the isolation of novel materials with distinctive structures and properties. Specifically, complex intermetallic compounds isolated by these techniques have shown promise in applications ranging from thermoelectrics^[5] to superconductivity.^[6]

We selected the copper–bismuth system owing to the large number of bismuth-containing superconductors with unusual properties; the $\text{Cu}_x\text{Bi}_2\text{Se}_3$ system with coincident superconductivity and topological insulating behavior^[7] is a notable example. There are no reported intermetallic compounds in the Cu–Bi binary system (Supporting Information, Figure S1).^[8] While there are scattered reports of superconducting amorphous Cu–Bi thin films^[9,10] and alloys,^[11] no structurally characterized intermetallic compound was ever isolated in these studies, and the reported transition temperatures vary substantially. As a consequence, little is known about the bonding and properties of solid-state systems containing exclusively copper–bismuth interactions, and structure–property relationships have been impossible to establish. Herein, we present the first binary compound in the Cu–Bi system, $\text{Cu}_{11}\text{Bi}_7$ (Figure 1), which is commensurately modulated and shows a bulk superconducting transition with $T_c = 1.36$ K.

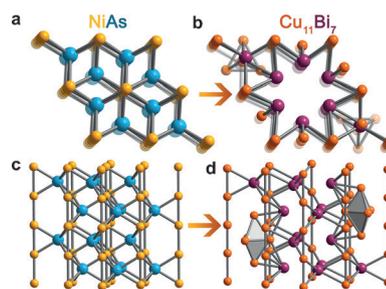


Figure 1. Comparison of the crystal structure of $\text{Cu}_{11}\text{Bi}_7$ (b, d) with a $2 \times 2 \times 2$ supercell of NiAs (a, c). Ni yellow, As blue, Cu orange, Bi violet. b) Viewing direction along the *c*-axis shows the ordered Cu vacancies in $\text{Cu}_{11}\text{Bi}_7$. d) Viewing direction along the diagonal of the *a*–*b* plane shows the trigonal bipyramids formed by the Cu atoms.

The new binary compound $\text{Cu}_{11}\text{Bi}_7$ was obtained in more than 90% yield by reaction of the elements at high pressure and temperature, approximately 6 GPa and 530 °C, for 1 hour. Upon completion of the reaction, the sample was rapidly

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cooled to ambient temperature and the pressure was released (see the Supporting Information for additional details). The compound created in this reaction, $\text{Cu}_{11}\text{Bi}_7$, is metastable at ambient pressure and temperature. The large family of compounds that is isolable after high-pressure synthesis, referred to as quenchable, can be readily investigated under ambient conditions. The quenchability of this new binary facilitated the structural and electronic characterization described below. The as-synthesized metallic pellet of $\text{Cu}_{11}\text{Bi}_7$ was employed for all characterization unless otherwise stated.

Mechanical grinding of the sample yielded small single crystals suitable for X-ray diffraction. Single crystal X-ray diffraction reveals a hexagonal sublattice with space group $P6_3/mmc$, lattice parameters of $a = 8.5941(2)$ Å and $c = 5.2542(2)$ Å, and additional supercell reflections around the main ones centered at a commensurate distance of $\frac{1}{3}a^* + \frac{1}{3}b^* + \frac{1}{2}c^*$. The commensurate supercell was solved using a (3+1)-dimensional crystallographic approach using the superspace group $Pm(a1/2\gamma)s$ with final unit cell parameters $a = 8.5907(4)$ Å, $b = 5.2542(3)$ Å, $c = 8.5931(5)$ Å, $\beta = 120.013(2)^\circ$, and a commensurate modulation vector $q = \frac{1}{3}a^* + \frac{1}{2}b^* + \frac{1}{3}c^*$. The pseudo-hexagonal cell allows for twinning along the [010] zone at 60 degrees rotation. Long-range ordering of the occupancies of the Cu and Bi sites are responsible for the modulations in the $\text{Cu}_{11}\text{Bi}_7$ structure. An understanding of this distinctive structure is facilitated by its similarity to the canonical NiAs structure type. Figure 1 depicts the relationship of the two structures along two different crystallographic directions. From this comparison, it is evident that the unique structure of $\text{Cu}_{11}\text{Bi}_7$ can be visualized as a commensurately modulated variation of the NiAs structure.

The structure of NiAs is composed of hexagonal close-packed (hcp) As atoms, where the octahedral holes are occupied by Ni atoms, thereby forming Ni chains along the c -axis. In $\text{Cu}_{11}\text{Bi}_7$, an ordered vacancy of one of these Cu chains generates one-dimensional pillars of hcp Bi atoms along the c -axis (Figure 1 b). The three-dimensional hcp structure of the Bi atoms is disrupted by Cu_5 trigonal bipyramids that alternate with Bi atoms along the c -axis (Figure 1 d). Within this structure, there are two columns where the Cu_5 structural motif alternates with a bismuth atom. Of these two columns, one is occupationally modulated along the diagonal modulation vector $\frac{1}{3}a^* + \frac{1}{2}b^* + \frac{1}{3}c^*$ while the second is disordered so that each atom is 50% occupied (Supporting Information, Figure S7). The Cu_5 bipyramid structure can, in fact, be envisioned as capped over all faces by Cu atoms, forming a larger Cu_{11} cluster that is apical-vertex-sharing with a dicapped trigonal prismatically coordinated Bi atom along the c -axis (Supporting Information, Figure S8). This larger structure is edge sharing in the a - b plane to form a Cu framework.

While the average Bi–Bi bond distance is similar throughout the structure ($d_{\text{ave}} \approx 3.44$ Å), there is a surprising variation in the average Cu–Cu bond distances, which fluctuate from $d_{\text{ave}} \approx 2.51$ Å between the equatorial Cu_5 atoms and the Cu chains to $d_{\text{ave}} \approx 3.04$ Å, between the apical Cu_5 atoms and the Cu chains. Interestingly, the shortest Cu–Bi bond (d_{ave}

≈ 2.76 Å) is between the apical Cu_5 atoms and a Bi from the pillar, implying that a stronger Cu–Bi interaction leads to a weaker Cu–Cu interaction.

We hypothesize that the structural segregation between the Cu framework and Bi pillars reflects the preference for full segregation of the elements at standard conditions. The unusual nature of this structural motif is reflected in a search of the Inorganic Crystal Structure Database (ICSD),^[12] which does not reveal any other examples of the $\text{Cu}_{11}\text{Bi}_7$ structure. While many NiAs-type compounds exhibit an occupational modulation of the transition metal atoms,^[13] to the best of our knowledge an ordered vacancy, giving rise to main group pillars, as seen in $\text{Cu}_{11}\text{Bi}_7$, has not been reported. Similar trigonal bipyramidal structures are formed in NiAs-type compounds $\text{Pd}_{13}\text{Tl}_9$ ^[14] and $\text{Fe}_{13}(\text{Ge}_{8.8}\text{Fe}_{0.2})$,^[15] although in both cases it is the main-group element that adopts this geometry, and not the transition metal. These observations suggest that the structure observed here is a unique derivative of the NiAs structure.

The prerequisite of employing high pressures in the preparation of this new compound inspired us to pursue a theoretical investigation to better understand its formation conditions. Coupling computation with experiment offers a powerful approach to enhance the search for new compounds by exploring an expanded phase space. To examine the effects of temperature and pressure in stabilizing the intermetallic compound, the formation free energy (ΔG_f) of the lowest energy ordered supercell, which has $C2/m$ symmetry, was estimated using density functional theory (DFT) calculations (see the Supporting Information for additional details). In accordance with the copper–bismuth binary phase diagram, at ambient pressure the formation energy of $\text{Cu}_{11}\text{Bi}_7$ is positive (55 meV per atom at 0 K), such that elemental decomposition is favored, even at high temperatures. With increasing pressure, the free energy of $\text{Cu}_{11}\text{Bi}_7$ decreases rapidly, until a negative formation energy is observed at approximately 12 GPa (0 K). From the DFT-calculated free energies, we are able to generate a temperature-pressure diagram depicting the calculated regions of negative formation free energy for $\text{Cu}_{11}\text{Bi}_7$ (Figure 2). The slope of the phase boundary is negative, indicating that the formation pressure of $\text{Cu}_{11}\text{Bi}_7$ is significantly reduced at higher temperatures. Indeed, the formation energy is merely 4 meV per atom at 800 K and 6 GPa, which is well within error bars inherent to DFT and can thus readily account for the stability of $\text{Cu}_{11}\text{Bi}_7$ at experimental conditions. Qualitatively, our calculations indicate that high pressure and temperature can stabilize $\text{Cu}_{11}\text{Bi}_7$ with respect to elemental decomposition.

Temperature-dependent electrical resistivity data were acquired to investigate the electronic behavior of $\text{Cu}_{11}\text{Bi}_7$. Resistivity ($\rho(T)$) measurements for the polycrystalline sample under zero applied magnetic field reveal a sharp superconducting transition (T_c) around 1.36 K (50% ρ_n , Figure 3 a). The small width of the transition ($\Delta T_c = 0.04$ K) indicates that the superconducting phase is indeed homogeneous. DFT calculations (see the Supporting Information) obtained a transition temperature of 1.4 K, in excellent agreement with the experimentally observed value of 1.36 K. As the strength of the applied magnetic field is

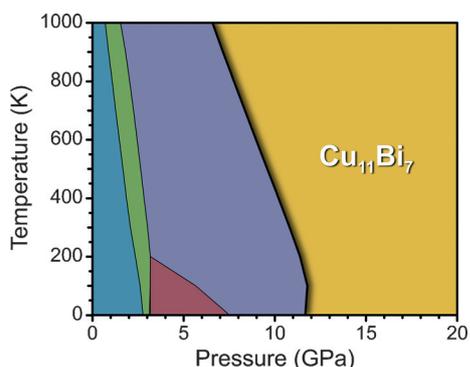


Figure 2. DFT-calculated temperature and pressure dependence of the formation Gibbs free energy (ΔG_f) of $\text{Cu}_{11}\text{Bi}_7$. $\text{Cu} + \text{Bi}$ ($R\bar{3}m$) teal, $\text{Cu} + \text{Bi}$ ($C2/m$) green, $\text{Cu} + \text{Bi}$ ($P4/ncc$) maroon, $\text{Cu} + \text{Bi}$ ($P2_1/m$) lilac. Fcc Cu and various elemental Bi allotropes are stable at low pressures. At ambient conditions, $\text{Cu}_{11}\text{Bi}_7$ is unstable with respect to decomposition into the elements (positive ΔG_f). However, with increased pressure and temperature, the intermetallic attains $\Delta G_f < 0$.

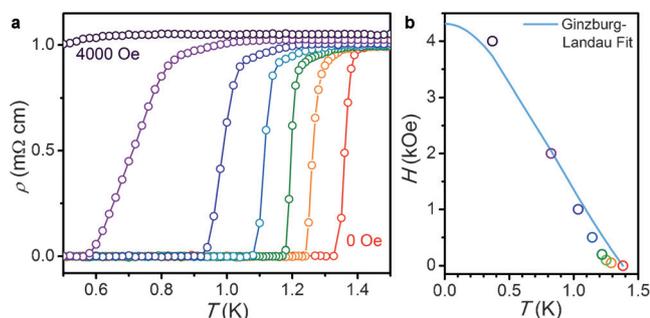


Figure 3. a) Temperature-dependent resistivity at various applied magnetic fields (from right to left: $H_{dc} = 0, 50, 200, 500, 1000, 2000,$ and 4000 Oe). Lines are drawn as guides for the eye. b) Critical field $H_{c2}(T)$ as a function of transition temperature (95% ρ_n). The solid blue line indicates fitting based on the Ginzburg–Landau (GL) law and yields $H_{c2}(0) = 4.3(3)$ kOe.

increased ($H_{dc} = 0\text{--}4000$ Oe), T_c is suppressed and broadened. An upper critical field $H_{c2}(0) = 4.3(3)$ kOe is determined from the fit of the critical field ($H_{c2}(T)$) versus T_c to the Ginzburg–Landau (GL) law (Figure 3b).^[16] The calculated $H_{c2}(0)$ is considerably higher than other bismuth intermetallic superconductors with comparable transition temperatures such as SrBi_3 ($T_c = 5.68$ K, $H_{c2}(0) = 0.92$ kOe),^[17] and PtBi_2 ($T_c = 1.21$ K, $H_{c2}(0) = 0.01$ kOe).^[18] The critical field is in accordance with the type-II superconducting transition-metal bismuthide NiBi_3 ($T_c = 4.0$ K, $H_{c2}(0) = 4.45$ kOe).^[19] The large ratio of upper critical field to the low critical temperature suggests that $\text{Cu}_{11}\text{Bi}_7$ is a type-II superconductor.

The nature of the superconductivity in $\text{Cu}_{11}\text{Bi}_7$ was further probed by heat capacity measurements (see the Supporting Information). The temperature dependence of the molar heat capacity ($C_p(T)$) under zero applied magnetic field exhibits a distinct superconducting transition beginning at 1.34 K and centered at 1.24 K (Supporting Information, Figure S11a). This feature corroborates the bulk nature of the superconducting transition and the onset temperature is in

excellent agreement with the T_c determined from electrical resistivity measurements. The electronic component of the molar heat capacity (C_{el}) was determined by subtracting the lattice contribution from the total molar heat capacity ($C_p(T)$). A plot of C_{el}/T versus T outlines the idealized heat capacity jump at $T_c \approx 1.24$ K, and yields a normalized value of $\Delta C_{el}/(\gamma T_c) \approx 1.44$ (Supporting Information, Figure S11b). This value closely matches the value of 1.43 predicted by BCS theory and further suggests that $\text{Cu}_{11}\text{Bi}_7$ is in the category of weak-coupling superconductors.

The foregoing results demonstrate the isolation and subsequent characterization of the first Cu–Bi intermetallic compound, $\text{Cu}_{11}\text{Bi}_7$, enabled by exploration of the high-pressure region of the Cu–Bi phase diagram. This new metastable compound is a BCS-type superconductor with a critical temperature of about 1.36 K. DFT calculations confirm that this phase is stabilized by high pressure. Other high-pressure phases in this system may offer exotic properties and deeper insight into the characteristics of Cu–Bi intermetallics. We expect that the success of this synthetic method will lead to other unique structures in the Cu–Bi system and will open up vast tracts of phase space for future synthetic research.

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