Cubine, a Quasi Two-Dimensional Copper–Bismuth Nanosheet

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ABSTRACT: We report on the discovery of a quasi two-dimensional copper–bismuth nanosheet from ab initio calculations, which we call cubine. According to our predictions, single layers of cubine can be isolated from the recently reported high-pressure CuBi bulk material at an energetic cost of merely ≈20 meV/Å², comparable to values to separate single layers of graphene from graphite. Our calculations suggest that cubine has remarkable electronic and electrochemical properties: It is a superconductor with a moderate electron−phonon coupling λ = 0.5, leading to \( T_c \approx 1 \) K, and can be readily intercalated with lithium with a high diffusibility, rendering it a promising candidate material to boost the rate capacity of current electrodes in lithium-ion batteries.

INTRODUCTION

Since the first successful exfoliating of graphene in 2004,¹−⁴ intense research has been devoted to the synthesis and characterization of two-dimensional (2D) materials. Meanwhile, various 2D materials have been discovered, ranging from graphene analogues such as silicene⁵−⁸ to phosphorene⁹ and borophene,¹⁰−¹⁵ transition metal dichalcogenides,¹⁶,¹⁷ transition metal carbides/nitrides,¹⁸,¹⁹ and transition metal carbynes.²⁰ Due to their diverse properties, 2D materials have been considered for many industrially relevant applications, including nanoelectronics, optoelectronics, and photonics.²¹−²⁴ but also in the field of energy storage. For metal-ion batteries, materials that can host \( \text{Li}^+ \) or \( \text{Na}^+ \) at high densities are of particular interest, a market currently dominated by carbonaceous (e.g., graphite and hard carbon) and layered materials (e.g., \( \text{LiCoO}_2 \)).²⁵ Two-dimensional materials are promising alternatives since they exhibit compelling ion transport and storage characteristics due to their open 2D channels and high specific surface areas with a large number of active sites.²⁶ Furthermore, since 2D materials only exhibit weak interlayer bonding via van der Waals (vdW) forces, unfavorable, large changes in their volumes during the intercalation and deintercalation of lithium ions are alleviated. Two-dimensional materials can also serve as functional substrates for incorporating active materials to improve the electrical and ionic conductivity of electrodes²⁷−²⁹ and are promising candidates for applications in nanostructured supercapacitors.²⁷,³⁰

Theoretical efforts to identify potential new 2D materials have been aimed at screening large databases of crystalline materials for low-dimensional structural patterns.²⁸−³⁰ Commonly, simple geometrical criteria such as large interlayer spacings are used to identify 2D units that could be separated through mechanical exfoliation. The recently discovered Cu–Bi intermetallics³¹−³⁵ have attracted considerable attention due to such low-dimensional structural features, including 1D channels and 2D voids.³¹−³³ Despite the strong immiscibility at ambient pressure,³⁴ Cu–Bi binary compounds have been known to form at high pressures since the early 1960s, exhibiting superconducting properties with a \( T_c \) between 1.33 and 1.40 K.³⁶ In 2016, a Cu₁₁Bi₇ compound was reported to form at moderate pressures, which crystallizes in a hexagonal structure with a \( T_c \) of 1.36 K.³¹ Recently, another high-pressure phase in the Cu–Bi system at the equiatomic composition, CuBi, was discovered with an orthorhombic unit cell.³₂,³³ Despite the dissimilarities in their crystal structures, both Cu₁₁Bi₇ and CuBi share a common structural motif, namely, the formation of voids to host the lone electron pairs (LEP) of the two bismuth atoms. In contrast to Cu₁₁Bi₇, which exhibits channels laced by LEP, CuBi forms a layered structure of alternating Cu, Bi, and LEP sheets. The formation of this low-density phase is the more surprising since such materials strongly violate the common perception that high-pressure phases have high densities with short, strong interatomic bonds.

Here we investigate the CuBi compound using ab initio methods to unravel the unique structural features of CuBi and reveal its two-dimensional character. Based on our calculations, layers of CuBi are held together by weak vdW forces, and we demonstrate that single nanosheets of CuBi can be separated from the bulk material at an extremely low cost in energy, one that is comparable to values required to exfoliate graphene from graphite. The dynamical stability of CuBi nanosheets show that they are viable as metastable phases and could be potentially used as a new class of building blocks in 2D heterostructures with compelling physical properties: they are superconducting with a \( T_c \approx 1 \) K, could be used to intercalate Li atoms at low voltages, and hence make an interesting new electrode for lithium-ion batteries.
4.263 Å, and a diamond structure at high pressures.37 Similarly, N2, a quasi 0D stable at ambient conditions, transforms into the dense cubic graphite, essentially consisting of layered graphene sheets and is the most prominent example for this behavior as carbon, where the penalty is expected for layered, vdW bonded materials. The therefore high-density polymorphs will be favored and a strong pV term becomes increasingly dominant, and therefore high-density polymorphs will be favored and a strong penalty is expected for layered, vdW bonded materials. The most prominent example for this behavior is carbon, where graphite, essentially consisting of layered graphene sheets and stable at ambient conditions, transforms into the dense cubic diamond structure at high pressures.37 Similarly, N2, a quasi 0D material at ambient pressure, turns into a polymeric phase at above 120 GPa,38 following the trend that the dimensionality of accessible polymorphs increases with pressure.

The recently discovered high-pressure CuBi material, however, poses a puzzling exception to this general rule, since pieces of evidence indicate that CuBi is in fact a layered material with a strong 2D character. Experimentally, CuBi crystallizes in an orthorhombic cell with Pmmn symmetry above 3.2 GPa, and its structure is shown in panel a of Figure 1 along the (010) direction. The atomic coordinates computed with the PBE functional are summarized in Table 1. According to our calculations, the lattice constants at 0 GPa are a = 5.204 Å, b = 4.263 Å, and c = 8.131 Å (see Table 2). While the values for a and b are in excellent agreement with experiments with errors of less than 0.5%, the c-vector is overestimated by roughly 3.3%.

**Table 1. Atomic Coordinates of Bulk CuBi Computed with the PBE Functional**

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff position</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
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<td>0.000</td>
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<tr>
<td>Bi2</td>
<td>2f</td>
<td>0.250</td>
<td>0.500</td>
<td>0.815</td>
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</tbody>
</table>

A very similar behavior is observed in graphite,39 where the interlayer distance is also severely overestimated, a first indication of the unusual behavior of CuBi. Furthermore, in both systems, this overestimation can be corrected by employing the LDA functional (due to its tendency of overbinding) or by using dispersion corrected PBE functionals as shown in Table 2. These findings clearly indicate that the interlayer interactions in CuBi are vdW mediated, a characteristic feature of layered 2D materials.

We can also see that CuBi is a layered material from a simple geometric argument. The main structural motif consists of layers of a buckled triangular sheet composed purely of Cu atoms in the a–plane, with two unique Cu–Cu bonds. Along the b-direction the bond length is 2.601 Å, whereas along the a-direction it is 2.580 Å. Bi atoms are attached to both sides of these Cu sheets along the c-direction. Two further geometrically inequivalent bonds are formed between Bi1 and Cu at distances of 2.716 and 2.969 Å, respectively, while Bi2 forms bonds with Cu at distances of 2.868 and 2.873 Å, respectively. No apparent bonds are formed between the Bi atoms, and all Bi–Bi distances are significantly larger than the sum of the covalent radii. In particular, the distance between the layers of Bi is 3.98 Å, clearly indicating that the bonding between the layers is neither covalent nor ionic. Furthermore, the electron localization function in Figure 1 shows no Bi–Bi bonds but instead reveals that stereochemically active LEP are interlaced between the Bi layers.

A detailed analysis of the lattice vibrations provides further evidence for the 2D character of CuBi. Figure 2a shows the phonon dispersion together with the path in the first Brillouin zone. We identify three specific features in the phonon band structure that are characteristic for quasi 2D materials. First, the lowest energy acoustic branch (yellow) shows a quadratic behavior as q → Γ along the in-plane directions X–Γ and Y–Γ, typical for 2D materials that exhibit a single flexural phonon branch with quadratic dispersion.40 Second, the very flat bands...
along \( \Gamma - Z \) with essentially zero dispersion can be directly attributed to extremely weak interactions between the layers. Third, the two lowest energy branches along \( \Gamma - Z \) are dominated by collective in-plane vibrations of the atoms in the \( a \)- and \( b \)-directions. This behavior is shown by the color coding based on the magnitude of the projected vibrational eigendisplacements along the three lattice vector components. The anisotropic compressibility and strong anharmonicity of CuBi is the fourth evidence for its 2D character. Figure 2b compares the structural parameters upon compression and expansion of CuBi with the recently discovered Cu11Bi7 phase.31 While the latter exhibits a roughly quadratic dependence of the energy on the volume, CuBi behaves strongly anharmonically, similar to graphite.41 The right panels in Figure 2b show the pressure dependence of the normalized unit cell volumes and the cell parameters upon pressure of CuBi.

Table 2. Lattice Parameters (Å) for CuBi and Graphite in Their Crystalline Phase (Columns 3–5) and as Isolated Layers of Cubine and Graphene (Columns 6 and 7) Using Various Exchange–Correlation Functionals\(^a\)

<table>
<thead>
<tr>
<th>method</th>
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<th>sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>cubine</td>
<td></td>
<td></td>
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<tr>
<td>PBE</td>
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<td>8.755</td>
</tr>
<tr>
<td>PBE(^{38})</td>
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</tr>
<tr>
<td>LDA(^{49})</td>
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<tr>
<td>exp(^{32})</td>
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<td>–</td>
</tr>
<tr>
<td>exp(^{34})</td>
<td>2.46</td>
<td>–</td>
</tr>
</tbody>
</table>

The last column contains the interlayer energies \( E_i \) (meV/Å\(^2\)). The following abbreviations were used for the various dispersion corrected PBE functionals: Grimme D2 (D2),\(^{43}\) Grimme D3 without (D3)\(^{44}\) and with (D3-BJ)\(^{45}\) Becke–Johnson dampening, Tkatchenko–Scheffler method with iterative Hirshfeld partitioning (TS-HP),\(^{46}\) and Steinmann’s density-dependent dispersion energy correction dDsC.\(^{47}\)

Figure 2. (a) Phonon dispersion of bulk CuBi along a path in the first Brillouin zone, computed with the PBE functional. The colors indicate the contribution of the vibrational eigenmodes along the three crystal lattices \( a \), \( b \), and \( c \). (b, left) Energy per atom as a function of volume, top for CuBi and bottom for Cu11Bi7; (right) evolution of the lattice parameters and the unit cell volume normalized to the ambient pressure values, for CuBi and Cu11Bi7 at the top and bottom, respectively.
introduced to separate the single sheets of cubine, followed by a relaxation of the atomic coordinates and the in-plane lattice vectors. The bond lengths in cubine only slightly change upon relaxation as shown in Figure 1b, with Cu–Cu distances of 2.599 Å along the a- and 2.579 Å along the b-direction, respectively. The Cu–Bi1 bonds change from 2.716 to 2.708 Å, and from 2.969 to 2.972 Å, respectively, while the Cu–Bi2 bonds decrease from 2.868 to 2.851 Å and from 2.873 to 2.835 Å, respectively. Figure 3a shows the phonon dispersion in the 2D Brillouin zone of this relaxed structure. No imaginary phonons are present, indicating that single sheets of cubine are dynamically stable. The color coding of the bands and the partial density of states show that two frequency regions can be clearly distinguished. The low-frequency regime below \( \approx 3 \) THz is strongly dominated by vibrations of the heavy Bi atoms, whereas the lighter Cu atoms contribute to the high-energy phonons.

To assess if cubine can be isolated, we computed the interlayer binding energy \( E_i \) between the individual sheets according to \( E_i = \frac{E_{\text{bulk}} - E_{\text{slab}}}{A} \), where \( E_{\text{bulk}} \) is the total bulk energy and \( A \) is the area spanned by the in-plane lattice vectors. \( E_{\text{slab}} \) is the energy of a single layer of cubine, evaluated by introducing a vacuum layer of 12 Å between the individual sheets. The PBE functional results in an extremely low value in \( E_i \) of merely 4 meV/Å². Using this value, a single cubine sheet has a positive formation energy of 68 meV/atom with respect to the elements. Since semilocal DFT does not account for vdW interactions, the real interlayer energy might be significantly higher. Indeed, our values of \( E_i \) by using functionals that (empirically) take into account dispersion energies, are overall higher than PBE and lie consistently in the range of \( \approx 15–30 \) meV/Å² (see Table 2). These values are close to the interlayer energies of graphite and other (quasi) 2D materials, and therefore strongly support the potential of exfoliating cubine from bulk in analogy to graphene.

Table 2 also provides two conclusive pieces of evidence that CuBi is indeed a layered material where cubine sheets interact with each other through vdW forces. First, all vdW functionals consistently predict lower c-vectors compared to PBE by 3–5%, which also agree significantly better with the experimental values. Second, evidence is directly given by the interlayer binding energies: since PBE does not describe any vdW interactions, the difference in the binding energy between a vdW functional and PBE, \( \Delta E_i = E_{i}^{\text{vdW}} - E_{i}^{\text{PBE}} \), can be directly attributed to the dispersion forces. The positive values in \( \Delta E_i \) for all vdW functionals show that in bulk CuBi the layers of cubine are held together by vdW forces.

In order to compare with available literature data, we screened the large 2D materials database at www.materialsweb.org for structures similar to cubine, but none of the 15 binary AB prototype structures matches its space group symmetry. However, two compounds have similar structural motifs of a...
core Cu sheet between layers of a second atomic species, namely, CuTe and CuBr. In contrast to cubine, CuBr has a completely planar Cu layer (space group $P4/nmm$), while CuTe exhibits a slightly different stacking geometry (space group $Pmnn$). Hence, the structure of cubine (space group $Pmnn$) is presumably novel, and we propose it to be added to the database as the 16th member of AB prototypes.

Similar to its bulk counterpart, cubine is metallic as illustrated by the band structure in Figure 3b with a rather low density of states (DOS) at the Fermi level. As expected, the strongest contributions at the Fermi level stem from the Cu 3d and Bi 6p states. The 2 Bi 6s electrons of the stereochemically active LEP are buried deep below the valence bands. Compared to the DOS of the bulk CuBi reported in ref 32, cubine in vacuum has a slightly lower contribution of Bi states at the Fermi level. We attribute this discrepancy in the DOS to the electronic interaction between the Bi atoms facing each other when the cubic sheets are stacked on top of each other in bulk CuBi. The gradual change of the electronic band structure due to quantum confinement as the bulk CuBi transform into isolated sheets of cubine is shown in Figure 3c. At every value of the $c$-vector, the in-plane cell vectors and all atomic coordinates were fully relaxed. The bands along $\Gamma$–S and S–Z become symmetric in the limit of large $c$-vectors (green), corresponding to the 2D sheet of cubine, while the bands of the bulk phase show an asymmetric dispersion (blue). The shaded area corresponds to the projected bands of the bulk structure onto the 2D Brillouin zone (where the bands were integrated along the out-of-plane direction in the reciprocal space) showing the effect of dispersion along the nonperiodic direction in the bulk phase.

This evolution of the electronic structure is also reflected in a change of the superconducting transition temperatures in the cubine nanosheet. Figure 4 shows the Eliashberg spectral function $\alpha^2 F(\omega)$ of cubine together with the integrated electron–phonon coupling parameter $\lambda(\omega)$ as a function of the phonon frequency $\omega$. There are two symmetrically distinct interstitial sites on both sides of a cubine sheet in one unit cell of Li$_x$CuBi. For $x = 0.25$ (i.e., one Li per cell), the most favorable adsorption sites are A and B, which are located between four Bi atoms and lead to adsorption energies per Li atom of 1.90 and 1.88 eV, respectively. Site C is energetically unfavorable and can only be occupied once both the A and B sites are completely filled at higher values of $x$. A full occupation of all sites results in Li$_7$CuBi, and a potential gravimetric charge density of 192.92 mAh g$^{-1}$. Figure 5a shows the lowest energy adsorption geometries together with the change in adsorption energies as a function of surface coverage.

Due to their large surface areas, 2D materials such as graphite have recently attracted interest as additives to enhance the performance of electrodes in metal-ion batteries. Here, we investigate the potential of using cubine sheets in lithium-ion batteries by studying the adsorption of Li atoms directly on its surface. We identified three symmetrically distinct sites on cubine where Li can be deposited, shown in the top right inset of Figure 5a. We systematically explored all possible decorations of these three sites on both sides of a cubine sheet in one unit cell of Li$_x$CuBi. For $x = 0.25$ (i.e., one Li per cell), the most favorable adsorption sites are A and B, which are located between four Bi atoms and lead to adsorption energies per Li atom of 1.90 and 1.88 eV, respectively. Site C is energetically unfavorable and can only be occupied once both the A and B sites are completely filled at higher values of $x$. A full occupation of all sites results in Li$_7$CuBi, and a potential gravimetric charge density of 192.92 mAh g$^{-1}$. Figure 5a shows the lowest energy adsorption geometries together with the change in adsorption energies as a function of surface coverage.

In practical energy storage applications, the kinetics of the adsorbed species on a surface is an important factor in the rate of charge/discharge. Hence, we computed the diffusion barriers of Li along the geometrically distinct paths on the cubine sheet (Figure 5b). The lowest barrier was found for the pathway A–B with a height of merely 0.13 eV, which is 40% lower than the barrier between the two most stable adsorption sites of Li on graphene. Since the A–B sites form a network on the surface connected through these low energy barriers, we expect that the Li atoms can diffuse at a high rate on the surface. The energy profile for the paths A–C and B–C show that the C site is indeed a stationary saddle point (between A–A and B–B sites), which only transforms into a local minimum once the A and B sites are occupied.

The very low interlayer binding energy, the large spacing of 3.98 Å (graphite, 3.35 Å) between the sheets, and the low diffusion barriers of Li on cubine also render bulk CuBi potentially an attractive candidate as a metal intercalation electrode. There are two symmetrically distinct interstitial sites per cell (inset of panel i, Figure 6a) with each 2-fold degeneracy between the cubine layers that can host four guest atoms in total. By fully occupying these sites with Li, Na, Mg, and Al, gravimetric (and volumetric) capacities of 96.46 mAh g$^{-1}$ (493.25 mA h/mL), 92.45 mAh g$^{-1}$ (472.75 mA h/mL), 184.27 mAh g$^{-1}$ (942.27 mA h/mL), and 274.51 mAh g$^{-1}$ (1403.72 mA h/mL) could be potentially achieved, respectively. Although the gravimetric capacities of bulk CuBi are rather moderate, the volumetric capacities are close to values of commercially used anode materials such as graphite (550 mA h/mL). Besides a high capacity, there is an increasing demand for electrode
materials with high rate capacities to improve battery power and to reduce the (re)charge time. To assess these charge/discharge and ion diffusion properties, we investigated the lithiation electrochemistry of CuBi. There are two intermediate phases on the CuBi−Li convex hull, where the end points are given by CuBi and elemental metallic Li, as shown in panel I of Figure 6a: Li_{x}CuBi and LiCuBi. The corresponding voltage profile is shown in panel ii, with values in a fairly low range of 0.18−0.34 V, indicating that this material is more suitable as an anode material. During the whole lithiation process, the CuBi backbone remains completely intact with only a slight sliding of the cubine layers against each other around the concentration Li_{0.5}CuBi (see panel iii in Figure 6a).

Furthermore, the interlayer diffusion of the Li atoms was investigated by computing the barriers along the geometrically distinct paths between the cubic layers (Figure 6b). The lowest among all barriers was found for the transition between the symmetrically equivalent 1 and 1″ sites with a value of merely 0.12 eV, which is even lower than the lowest barrier for the isolated cubine sheet. With all transition barriers at hand, a kinetic Monte Carlo simulation was carried out to estimate the lithium-ion diffusivity $D$. The values of $D$ as a function of temperature are shown in Figure 6b(iii), calculated using a...
typical attempt frequency of $\nu = 10^{13}$ s$^{-1}$. We find a superior Li diffusivity of $3.8 \times 10^{-3}$ cm$^2$/s at room temperature, more than 1 order of magnitude higher than state-of-the-art anodes (graphite, $D = 10^{-6} - 10^{-11}$ cm$^2$/s; Li$_4$Ti$_5$O$_{12}$ (LTO), $D = 10^{-11} - 10^{-12}$ cm$^2$/s) and cathodes (LiCoO$_2$ (LCO), $D = 10^{-9} - 10^{-10}$ cm$^2$/s; LiFePO$_4$ (LFP), $D = 10^{-9} - 10^{-11}$ cm$^2$/s). This remarkable diffusivity renders CuBi a high-rate material that is capable of conducting Li faster than any known electrode material to date. Considering the high volumetric capacity together with the intriguing Li conductivity at relatively low cost, CuBi is a promising candidate to be used on its own in an anode for applications where space is limited and a high charge/discharge rate is required in electrical energy storage, e.g., in electric vehicles and for peak load regulations of smart power grids. On the other hand, cubine with its large surface area and high number of active sites could be used as a component in composite anode and cathode materials (such as graphene) to improve their performance, e.g., by increasing the rate capacity$^3$ and cyclability.

In summary, we report on the discovery of a novel quasi 2D sheet, cubine. We present many pieces of compelling evidence to demonstrate that CuBi is indeed a layered material with weak vdW interactions between single cubine sheets. Since the interlayer energy is comparable to graphene, we predict that single sheets of cubine can be exfoliated from CuBi using similar techniques used to isolate graphene from graphite. As a single sheet, cubine is metallic with a moderate electron–phonon coupling, leading to superconducting transition temperatures in the range of around 0.6–1 K. Since it is dynamically stable, cubine can readily serve as a building block for heterostructured 2D materials, and its large surface area offers potential active sites for adsorbates such as Li atoms. The low energy barriers between the A and B sites allows a high diffusion of Li on cubine. Furthermore, we demonstrate that the bulk CuBi can be readily intercalated with lithium with a high ion diffusivity, rendering it a promising candidate for energy storage applications.

### METHODS

Density functional theory (DFT) calculations were carried out within the projector augmented wave (PAW) formalism$^{61}$ as implemented in the VASP$^{63-64}$ package. Unless otherwise noted, we employed the Perdew–Burke–Ernzerhof (PBE) approximation$^{85}$ to the exchange–correlation potential. A plane-wave cutoff energy of 400 eV was used with a sufficiently dense $k$-point mesh to ensure a convergence of the total energy to within 1 meV/atom. Both the atomic and cell parameters were simultaneously relaxed until the maximal force was less than 2 meV/Å and stresses less than 0.01 GPa. The structures were fully relaxed with the correct energy derivatives components were less than 2 meV/Å and stresses less than 0.01 GPa.

Phonon calculations were carried out with the frozen phonon approach as implemented in the PHONOPY package$^{67}$ using sufficiently large supercells for converged thermal properties. To compute the vibrational contribution to the density of states, a dense mesh of $30 \times 30 \times 30$ was used to sample the irreducible Brillouin zone.

The Quantum Espresso package$^{68}$ was used to compute the phonon-mediated superconducting properties. We used norm conserving FHI pseudopotentials and a plane-wave cutoff energy of 150 Ry. The Allen–Dynes modified McMillan’s approximation of the Eliashberg equation$^{69}$ was used to estimate the superconducting temperature:

$$T_c = \frac{\Theta_{10}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]$$  

(1)

where $\mu^*$ is the Coulomb pseudopotential, $\lambda$ is the overall electron–phonon coupling strength computed from the frequency-dependent Eliashberg spectral function $\sigma F(\omega)$, and $\Theta_{10}$ is the logarithmic average phonon frequency. A $4 \times 4 \times 1$ $q$-mesh was used together with a denser $32 \times 32 \times 1$ $k$-mesh for the 2D $Pmna$ structure, resulting in a well-converged superconducting transition temperature $T_c$. A value of $\mu^* = 0.10–0.13$ was employed, which was shown to give values of $T_c$ in excellent agreement with experimental results for the Cu$_4$Bi$_4$ superconductor.$^{31}$

The Li adsorption process on the cubic single layer was computed using the non-equilibrium phase search method (NEPS)$^{70-72}$ by exploring geometrically distinct Li/vacancy configurations on all possible adsorption sites of the cubic surface at different compositions (Li/vacancy ratios). Starting with the cubic unit cell (Cu$_4$Bi$_4$) which has a total of eight empty sites where Li ions can adsorb, we generated all symmetrically distinct configurations using Enum$^{73,74}$ for a series of compositions Li$_x$Cu$_{4-x}$Bi$_4$ (0 < $x$ < 2, $\square$ denoting vacancies). The total energies of all configurations were evaluated with the DFT settings described earlier. We also adopted the vdW-DF functional (optB88$\gamma$),$^{75}$ which employs a self-consistent van der Waals (vdW) correction. At each composition $x$ the adsorption energy was computed according to

$$E_{ads} = \frac{E(\text{Li}, \text{CuBi}) - xE(\text{Li}) - E(\text{CuBi})}{x}$$  

(2)

where the reference energy $E(\text{Li})$ of a single Li was evaluated in vacuum using a $10 \times 10 \times 10$ Å supercell.

To simulate the lithiation process of bulk CuBi, the conventional cell was used to explore geometrically distinct potential Li sites between the cubic layers. All symmetrically inequivalent occupation of these sites was used as input structures and relaxed with respect to the atomic and cell variables using the PBE functional, resulting in energies as a function of Li/vacancy ratios, i.e., the Li concentrations in Li$_x$Cu$_4$Bi$_4$. The formation energies were evaluated according to the following reaction: CuBi + xLi $\rightarrow$ Li$_x$CuBi. The lithiation convex hull was constructed from the lowest formation energies at every composition, and only those intermediate phases which lie on the hull were considered, using metallic Li as a reference. The average lithiation/delithiation reaction voltage relative to Li/Li$^+$ is given by the negative of the reaction free energy per Li$^{76}$:

$$\nu = \frac{\Delta G_i}{F \Delta N_{Li}}$$  

(3)

where $F$ is the Faraday constant, $\Delta N_{Li}$ is the amount of Li added/removed, and $\Delta G_i$ is the (molar) change in free energy of the reaction. The enthalpic ($\Delta H_{ads}$) contribution to $G$ is of the order of 0.1 eV per Li at atmospheric pressure and can be safely ignored, while the entropic contribution to the voltage was assumed to be small and was therefore neglected.$^{77}$ Hence, the total DFT $T = 0$ K internal energies ($E$) were used to approximate G:

$$\Delta G \approx \Delta E = E(\text{Li}, \text{CuBi}) - E(\text{CuBi}) - xE(\text{Li}_{\text{metal}})$$  

(4)
where $E$(Li,CuBi), $E$(CuBi), and $E$(Li$_{1.5}$) are the total energies of Li$_2$BiCu, BiCu, and elemental Li, respectively. The lithium-ion diffusivity was studied using kinetic Monte Carlo (KMC) simulations using the Materials Interface package MINTY$^{6,9}$ based on barriers computed through the climbing image nudged elastic band (cNEB) approach as implemented in the VASP TST package.$^{60-62}$

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