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## Potassium-activated anionic copper and covalent Cu-Cu bonding in compressed K-Cu compounds

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#### ABSTRACT

Elemental copper and potassium are immiscible under ambient conditions. It is known that pressure is a useful tool to promote the reaction between two different elements by modifying their electronic structure significantly. Here, we predict the formation of four K–Cu compounds ( $K_3Cu_2, K_2Cu, K_5Cu_2$ , and  $K_3Cu$ ) under moderate pressure through unbiased structure search and first-principles calculations. Among all predicted structures, the simulated x-ray diffraction pattern of  $K_3Cu_2$  perfectly matches a K–Cu compound synthesized in 2004. Further simulations indicate that the K–Cu compounds exhibit diverse structural features with novel forms of Cu aggregations, including Cu dimers, linear and zigzag Cu chains, and Cu-centered polyhedrons. Analysis of the electronic structure reveals that Cu atoms behave as anions to accept electrons from K atoms through fully filling 4s orbitals and partially extending 4p orbitals. Covalent Cu–Cu interaction is found in these compounds, which is associated with the *sp* hybridizations. These results provide insights into the understanding of the phase diversity of alkali/alkaline earth and metal systems.

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#### INTRODUCTION

Alkali/alkaline earth and noble metal-based compounds have attracted considerable interest because of their interesting and sometimes extraordinary properties. For example, elemental Au and Cs are both good metals, but the CsAu compound has semiconductor behavior.<sup>1,2</sup> This abnormal behavior is attributed to the departure of both elements from nearly free electron metals, which leads to the ionization of Cs<sup>+</sup> and Au<sup>-</sup> in the compound.<sup>3</sup> Similarly, Cs<sub>2</sub>Pt is a

transparent compound with a sizable bandgap, described in terms of  $Cs^+$  and  $Pt^{2-}$  ions.<sup>4</sup> The high-pressure compound  $K_2Ni$  also exhibits a semiconducting ground state with an indirect bandgap.<sup>5</sup> In these compounds, the valence electrons of alkali metals are partially transferred to the transition metal and fill up the *d* orbitals of the latter. The induced ionic interaction stabilizes the system and opens a bandgap. Depending on the bond order, the transition metal anions may aggregate in different forms.<sup>6</sup> Ionic  $[M-M]^4$  (M = Cu, Ag, and Au) dimers were found in Yb<sub>2</sub>Cu<sub>2</sub>In,<sup>7</sup> Ca<sub>5</sub>Ag<sub>3</sub>,<sup>8</sup> and Ca<sub>5</sub>Au<sub>4</sub><sup>9</sup> in

which noble metal elements behave like main group *p*-elements and are bounded by  $\sigma$  bonds. Zigzag silver chains were identified in CaAg and SrAg.<sup>10</sup> Linear platinum chains were found in both BaPt<sup>11</sup> and Li<sub>2</sub>Pt<sup>12</sup> with prominent covalent characteristics. In particular, BaPt and Li<sub>2</sub>Pt are considered as quasi-2D Dirac semimetals with  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals of the Pt atom forming a Dirac cone at the *k*-point in the Brillouin zone (BZ).<sup>13</sup>

Copper occupies a position between nickel and zinc in the Periodic Table of elements. Its  $3d^{10}4s^1$  valence configuration can have multiple oxidation states, which are associated with a rich variety of copper compounds. The common oxidation states of copper are +1 and +2, but higher oxidation states were also reported, e.g., +3 in KCuO<sub>2</sub> and K<sub>3</sub>CuF<sub>6</sub> (+3) and +4 in Cs<sub>2</sub>CuF<sub>6</sub>.<sup>14,15</sup> Cupric oxide (CuO), in particular, has been investigated as a multiferroic material with a topological arrangement of Cu (+2).<sup>16</sup> On the other hand, Cu's low electronegativity (1.90 Pauling scale) means that its negative oxidation states are uncommon. To date, the only known case appears to be the [Cu-Cu]<sup>4-</sup> dimers in Yb<sub>2</sub>Cu<sub>2</sub>In.<sup>7</sup> However, pressure has a profound effect on the chemical reactivity and can create compounds of elements that are immiscible at ambient pressure.<sup>17-19</sup> For instance, Cu<sub>11</sub>Bi<sub>7</sub> and CuBi compounds have been synthesized at high pressure and Cu<sub>11</sub>B<sub>7</sub> has been found to be superconducting with a critical temperature of 1.36 K,<sup>20,21</sup> while theory predicts that Cu<sub>2</sub>Bi is also stable and has a  $T_c$  of 2 K at high pressure.<sup>22</sup> Snider and Badding<sup>23</sup> synthesized K-Cu compounds by compressing the mixtures of K and Cu in the diamond anvil cell (DAC) up to about 50 GPa. The synthesized K-Cu phases were found to be stable over a pressure range of 9.5-32.5 GPa and found to be stable down to 5 GPa. Crystallinity was identified for these phases by in situ x-ray diffraction (XRD) measurement, but the structures have not been resolved. In this work, we systematically perform the structural search for the K-Cu system within 0-100 GPa combining the unbiased global optimization method and first-principles calculations. Four new phases, e.g., K<sub>3</sub>Cu<sub>2</sub>, K<sub>2</sub>Cu, K<sub>5</sub>Cu<sub>2</sub>, and K<sub>3</sub>Cu, are predicted to be stable in a moderate pressure range. In particular, the simulated XRD pattern of K<sub>3</sub>Cu<sub>2</sub> matches well with one of the synthesized K-Cu phases. In the predicated compounds, the copper atom behaves like a *p*-block element in which the frontier levels are partially filled 4p bands and induces metallicity. The prediction of these new compounds, with one confirming previous experiment, adds several members to the compounds formed between potassium and transition metals, including K-Ag,<sup>24-26</sup> K-Au,<sup>27-29</sup> K-Fe,<sup>30,31</sup> K-Ni,<sup>32</sup> K-Ir,<sup>33</sup> and K-Hg.<sup>34</sup>

#### COMPUTATIONAL DETAILS

Crystal structures of various K–Cu compounds were searched in a wide stoichiometric space using two global structure search methods. The first set of search was carried out with variable compositions in unit cells containing up to 40 atoms at 4 targeted pressures (0, 20, 50, and 100 GPa) using the evolutionary algorithm based USPEX package.<sup>37,38</sup> The second batch of search was performed with fixed compositions at same pressures using the swarm intelligencebased CALYPSO package.<sup>39,40</sup> The ratio of K:Cu in the stoichiometry was set as 3:1, 5:2, 2:1, 3:2, 1:1, 1:2, and 1:3. The relative stability of each considered stoichiometry was evaluated by calculating the formation enthalpy of the most stable structure in the group. The

formation enthalpies ( $\Delta H$ ) for all K–Cu phases were calculated using the equation  $\Delta H(K_x Cu_{1-x}) = H(K_x Cu_{1-x}) - xH(K) - (1-x)H(Cu)$ . Here,  $H(K_xCu_{1-x})$  represents the enthalpy for each composition at a given pressure; H(Cu) is the enthalpy of solid Cu, and H(K) is the enthalpy of solid K. Due to the phase transitions of potassium under high pressure, bcc-K [space group (S.G.): Im-3m, 0-10 GPa], fcc-K (S.G.: Fm-3m, 10-19 GPa), oP8-K (S.G.: Pnma, 19-62 GPa), tI4-K (S.G.: I41/amd, 62-80 GPa), and oC16-K (S.G.: Cmca, 80-100 GPa) were chosen as the reference phases under pressures. The enthalpy differences of K phases relative to the ambient bcc phase are calculated and plotted in Fig. S1 as a function of pressure, which is in good agreement with previous report<sup>41</sup> and establishes the reliability of the present calculations. Elemental Cu retains the fcc structure in the pressure range of interest, which is used as the reference phase for Cu. The crystal structures of all K-Cu compounds were fully relaxed, and the properties were calculated in the framework of density functional theory (DFT)<sup>42</sup> using the Vienna Ab initio simulation package (VASP)<sup>43</sup> and projector-augmented-wave (PAW)<sup>44</sup> potentials. The exchange and correlation of electrons were treated in the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional.<sup>45</sup> A plane-wave basis set with a cutoff energy of 500 eV is chosen for the wavefunctions. A dense Monkhorst-Pack k-point grid<sup>46</sup> of spacing  $2\pi \times 0.03$  Å<sup>-1</sup> is used for the BZ sampling to ensure the convergence of total energy to less than 1 meV per atom. Phonon calculations were carried out by using finite displacement methods as implemented in the PHONOPY code.<sup>47,48</sup> Crystal structures and charge density difference (CDD)<sup>49</sup> were visualized using the VESTA package.50

#### **RESULTS AND DISCUSSIONS**

The configuration space of K-Cu compounds is explored by extensive structural search. The low-enthalpy structures selected in each stoichiometry are subject to finer structural optimization and enthalpy calculation from which a global stability tie line (convex hull) is established. The convex hulls obtained at different pressures are presented in Fig. 1(a) and Fig. S2. At ambient pressure, all predicted K-Cu compounds have positive formation enthalpies (Fig. S2), which is consistent to the absence of stable K-Cu phases in nature. The first stable K-Cu compound appears at 10 GPa [Fig. 1(a)]. K<sub>3</sub>Cu<sub>2</sub> is thermodynamically stable with respect to elemental K and Cu with a negative formation enthalpy of -0.054 eV/atom. With increasing the pressure, K<sub>3</sub>Cu falls on the convex hull at about 20 GPa, but K<sub>2</sub>Cu and K<sub>5</sub>Cu<sub>2</sub> appear at 30 GPa. Interestingly, all predicted K-Cu structures will become unstable again at higher pressures. Pressure induced formation and subsequent decomposition of compounds have been observed before, in particular, in binary intermetallic alloys such as Cs-Au<sup>51</sup> and lanthanum alloys.<sup>52</sup> The ranges of thermodynamic stability for the predicted compounds are presented in Fig. 1(b). K<sub>3</sub>Cu<sub>2</sub> (S.G.: P6<sub>3</sub>/mmc), K<sub>2</sub>Cu (S.G.: Cmcm), K<sub>5</sub>Cu<sub>2</sub> (S.G.: C2/m), and K<sub>3</sub>Cu (S.G.: I4/mmm) are stable within the pressure range of 8.5-32, 30-72.5, 22.5-42, and 10.5-30.5 GPa, respectively, with no phase transitions identified. Dynamical stabilities of the predicted K-Cu compounds were examined by calculating the phonon dispersion relations. The absence of imaginary phonon frequencies across the entire BZ (Fig. S3) confirms the dynamical stability of these structures under pressure.



FIG. 1. (a) Calculated convex hull of the K–Cu system in the pressure ranges of 10–50 GPa. Structures on the convex hull (solid symbols) are stable against decomposition into elemental K and Cu or other K–Cu phases. (b) Pressure range of stability for predicted K–Cu compounds. Different phases are separated by colors. (c) Simulated XRD patterns for K–Cu compounds at 20 GPa in comparison with the experimental results (compressed mixture with the K–Cu ratio of 2:1) in Ref. 23. x-ray wavelength used is 1.5406 Å.

Snider and Badding synthesized K-Cu compounds<sup>23</sup> by compressing stoichiometric K-Cu mixtures with K-Cu ratios of 2:1, 1:1, and 2:1 in the diamond anvil cell. The XRD profiles obtained for each of the mixtures show likely formation of crystalline phases, but it has been challenging to solve the structures due to the complexity of the K-Cu phase diagram at high pressure. By simulating and comparing the XRD patterns for the predicted K-Cu compounds, we are able to solve one of the experimental phases. The simulated XRD pattern of K<sub>3</sub>Cu<sub>2</sub> shows a perfect match with the experimental one for the 2:1 K–Cu mixture [Fig. 1(c)]. The calculated *d*-spacing values for the K<sub>3</sub>Cu<sub>2</sub> structure are 4.227, 2.493, 2.437, 2.111, 2.030, 1.743, and 1.559 Å, which agree well with the experiment. The lower bound of the stability region for K<sub>3</sub>Cu<sub>2</sub> is 9.5 GPa [Fig. 1(c) and Fig. S4], also consistent with the synthesis conditions. Yet, the structures for the other two mixtures cannot be solved since the present calculation shows that no K-Cu phases on the copper-rich side should be thermodynamically stable. Nevertheless, the confirmation of one experimental phase validates the structure search, encouraging new efforts to realize other predicted compounds in the near future

The crystal structures of predicted K-Cu compounds are shown in Fig. 2. The optimized lattice parameters and atomic positions for each structure are documented in Tables S1 and S2. The structures of K-Cu compounds share a common motif in which K atoms form honeycomb layers and accommodate Cu in the vertices. The honeycomb layers are planar in K<sub>2</sub>Cu, K<sub>5</sub>Cu<sub>2</sub>, and K<sub>3</sub>Cu but puckered in K<sub>3</sub>Cu<sub>2</sub> (Fig. S5). In hexagonal K<sub>3</sub>Cu<sub>2</sub> [Fig. 2(a)], each K atom is coordinated by other eight K atoms with K-K separations of 3.0–3.1 Å,<sup>53</sup> forming a hexagonal tunnel-like sublattice. The Cu atoms in the vertices are homonuclearly bonded and form linear infinite  $Cu_{\infty}$  chains propagating along the *c* direction. The closest Cu-Cu separation is 2.25 Å, shorter than the value in elemental Cu (2.45 Å), indicating stronger Cu-Cu interaction in K<sub>3</sub>Cu<sub>2</sub>. Metal chains with similar geometry were previously known in BaPt<sup>1</sup> and Li<sub>2</sub>Pt.<sup>12</sup> K<sub>2</sub>Cu has similar honeycomb layers but with a modulated stacking of the layers, resulting in zigzag shaped Cu<sub>∞</sub> chains in the channels. The K–K contacts vary between 2.74 and 3.04 Å, and Cu–Cu bond distances are all 2.53 Å. Besides the two neighboring Cu atoms, each Cu atom is coordinated by a bicapped trigonal prism of K<sub>8</sub> with K–Cu separations ranging from 2.70 to 3.04 Å, corresponding to a coordination number of 10 (2 + 8). In terms of crystal geometry, K<sub>2</sub>Cu is very similar to K<sub>2</sub>Ni,<sup>5</sup> which is also a high pressure phase, and the zigzag Cu<sub>∞</sub> chains resemble the zigzag silver chains in CaAg and BaAg.<sup>10</sup>

The potassium sublattice in K5Cu2 is consisting of a series of honeycomb sheets with trigonal K7 units. The sheets are filled by diatomic Cu<sub>2</sub> units and stacked together in ABA ... A sequence [Fig. 2(c)]. The K–K bondlengths are in the range of 2.80–2.90 Å. The Cu<sub>2</sub> units are located at the center of the bicapped hexagonal prisms K<sub>20</sub>. These Cu<sub>2</sub> units can be best described as dimeric Zintl anions, taking advantage of electrons transferred from nearby K atoms. Anionic Cu<sub>2</sub> has been observed in Ca<sub>5</sub>Cu<sub>3</sub>,<sup>54</sup> while similar Au<sub>2</sub> and Hg<sub>2</sub> anions were reported in Ca<sub>5</sub>Au<sub>4</sub><sup>9</sup> and Ca<sub>3</sub>Hg<sub>2</sub> as well. The Cu-Cu distance in the Cu<sub>2</sub> dimer in K<sub>5</sub>Cu<sub>2</sub> is 2.42 Å, slightly shorter than that in *fcc*-Cu (2.45 Å). K<sub>3</sub>Cu has a tetragonal Cu<sub>3</sub>Ti-type structure with the *I*4/*mnm* space group.<sup>56</sup> The same stoichiometry has been known in intermetallic alloys including Li<sub>3</sub>Au,<sup>5</sup> Rb<sub>3</sub>Ir,<sup>58</sup> Ir<sub>3</sub>K,<sup>33</sup> and K<sub>3</sub>Ag.<sup>24</sup> The crystal structure of K<sub>3</sub>Cu can be viewed as a three dimensional extension of alternating close-packed [CuK<sub>8</sub>] and [KK<sub>8</sub>] hexahedra [Fig. 2(d)]. The K network is formed by interconnected lantern-like K14 cages constructed by edge sharing K4 rhombi. The K-K separations in K3Cu are all identical, with the length of 2.89 Å, about 9% shorter than those in fcc-K. Single Cu atoms occupy the centers of the K14 cages with Cu-K separations of 2.89 Å (×8), 3.19 Å (×4), and 3.59 Å (×2). The presence of cage structure in K<sub>3</sub>Cu indicates a larger radius of the Cu anion, which is confirmed by the analysis on the charge difference density (see below). In short, the geometry change of Cu atoms in K-Cu systems follows a sequence of linear chains (K<sub>3</sub>Cu<sub>2</sub>) at about 8.5-32 GPa, isolated Cu atoms (K<sub>3</sub>Cu) at 10.5-30.5 GPa, Cu<sub>2</sub> dimers (K<sub>5</sub>Cu<sub>2</sub>) at 22.5-42 GPa, and zigzag chains (K<sub>2</sub>Cu) at 30-72.5 GPa. Therefore, the trend of change in the K-Cu ratio under high pressure is K<sub>3</sub>Cu<sub>2</sub>



**FIG. 2**. (a) Crystal structure of  $K_3Cu_2$  in the  $P6_3/mmc$  space group with K at 4f (1/3, 2/3, 0.417) and 2d (1/3, 2/3, 3/4) and Cu at 2a (0, 0, 1/2) and 2b (0, 0, 3/4) sites. (b) Crystal structure of  $K_2Cu$  in the *Cmcm* space group with K and Cu atoms occupying 8g (0.831, 0.860, 3/4) and 4c (1/2, 0.902, 3/4) sites, respectively. (c) Crystal structure of  $K_5Cu_2$  in the *C2/m* space group with K occupying 2b (0, 1/2, 0), 4i (0.709, 1/2, 0.853), and 4i (0.579, 1/2, 0.299) sites and Cu occupying the 4i (0.876, 1/2, 0.435) site. (d) Crystal structure of  $K_3Cu$  in the *I4/mmm* space group with K locating at 2a (0, 0, 0) and 4d (1/2, 0, 1/4) sites and Cu locating at the 2b (1/2, 1/2, 0) site. All structures are optimized at 30 GPa.

to  $K_3Cu$  to  $K_5Cu_2$  and to  $K_2Cu,$  consistent with the clustering of Cu atoms.

To understand the electronic origin of the stability of Cu-K compounds, total density of states (DOSs), DOSs projected to orbitals, and band structures are calculated and shown in Figs. 3 and 4. All predicted Cu-K phases are found to be metallic with a finite DOS at the Fermi level ( $E_F$ ). The states at and across the Fermi level are dominated by Cu-p orbitals, together with small contributions from K-s orbitals. Clearly, this suggests that the 4p orbitals of Cu are partially filled, which is consistent with the anionic nature of Cu species in the compounds. For K<sub>3</sub>Cu<sub>2</sub>, the states around the Fermi level are primarily from the  $Cu-p_z$  states. Due to the linear arrangement of Cu chains along the *c*-axis, Cu-*p*<sub>z</sub> orbitals have significantly greater overlaps and energy dispersion than the geometrically equivalent  $Cu-p_x$  and  $Cu-p_y$  orbitals. Furthermore, the overlapping between Cu-s and Cu- $p_z$  states in (-4, -0.6) eV indicates the tendency of s-p mixing and covalent nature of Cu-Cu interactions, which is also reflected by the mixed distribution of Cu-s and Cu-p orbitals in the fat energy bands [Fig. 4(a)]. Covalent Cu-Cu interactions are quantified by the crystal orbital Hamiltonian population (ICOHP) and integrated crystal orbital Hamiltonian population (ICOHP) analyses [Fig. 3(a)]. The -ICOHP value for the Cu-Cu bond is 3.103 eV/pair. Strong bonding interaction can be observed below the Fermi level with bonding states throughout the region and minor antibonding states at (-2.3, -2.1) eV. The Cu-d states are fully submerged below the Fermi level  $(-5.0 \sim -2.1 \text{ eV})$  and nearly dispersionless, corresponding to fully filled orbitals  $(3d^{10})$ . On the other hand, significant dispersion of bands with Cu  $4p_z$  frontier

J. Chem. Phys. **154**, 134708 (2021); doi: 10.1063/5.0045606 Published under license by AIP Publishing states presents near the Fermi level along the reciprocal lines parallel to  $c^*$  ( $\Gamma$ -A, H-K, and M-L). This characterizes the formation of linear chains of Cu in K<sub>3</sub>Cu<sub>2</sub> and strong Cu–Cu interaction along the [0 0 1] direction. A similar band structure and bonding feature have been shown for the linear chain of Pt in BaPt<sup>11</sup> and Li<sub>2</sub>Pt.<sup>12</sup>

In K<sub>2</sub>Cu, 4s bands of Cu are compressed in a narrower energy range due to weaker Cu-Cu interactions within the zigzag chains. These bands split into three energy ranges of (-5.6, -3.8) eV, (-3.7, -3.8) eV, (-3.8, -3.8) eV, (-3-3) eV, and (-2.5, -1) eV roughly for bonding, non-bonding, and anti-bonding blocks. The Cu 4p bands occupy (-1, 1.5) eV with the contributions of  $p_y > p_z > p_x$  at the Fermi level. Noted that the partial covalent Cu-Cu interaction induces the dispersion in the 4p bands, which also mixes slightly with the 4s band between -2.5 and -1.0 eV. The Cu-Cu bonding strength in K<sub>2</sub>Cu is weaker than that in K<sub>3</sub>Cu<sub>2</sub> due to a longer bondlength in zigzag chains. This feature is quantified by a smaller -ICOHP value, i.e., 2.67 eV/pair. The Cu 3d bands are located in the energy region (-5.1, -2.0) eV and nearly flat along  $\Gamma$ -Z, T-Y, and X-U directions. Again, the Cu 3d orbitals are fully occupied, and therefore, no dispersion or orbital mixing is expected. Same as K<sub>3</sub>Cu<sub>2</sub>, Cu atoms in K<sub>2</sub>Cu behave like a p-block metal with partially filled 4p frontier levels. In K<sub>5</sub>Cu<sub>2</sub>, an even smaller composition of Cu results in less dispersion of the 4s bands, with completed separated bonding, non-bonding, and antibonding blocks [(-5.5, -4.3) eV, (-3.8, -3) eV, and (-2.7, -2) eV]. The Cu 4p bands appear mostly between -1.0 and 1.5 eV, whereas only the bottom portion is occupied. This gives rise to the metallic property for K<sub>5</sub>Cu<sub>2</sub>, while the contributions from  $p_x$ ,  $p_y$ , and  $p_z$ orbitals are almost equal at the Fermi level. In general, the electronic





structure of the Cu<sub>2</sub> dimer in K<sub>5</sub>Cu<sub>2</sub> is similar to Cu<sub>2</sub> in Yb<sub>2</sub>Cu<sub>2</sub>In,<sup>7</sup> Au<sub>2</sub> in Ca<sub>5</sub>Au<sub>4</sub>,<sup>9</sup> and Pt<sub>2</sub> dimers in La<sub>2</sub>Pt<sub>2</sub>In.<sup>59</sup> The covalent interaction in the Cu<sub>2</sub> dimer is quantified by the -ICOHP value of 3.283 eV/pair. K<sub>3</sub>Cu is the only K–Cu compound that does not have aggregated Cu atoms. In this structure, Cu atoms are distributed in the

K sublattice and anionized by electrons transferred from the latter. Bader charge analysis establishes the amount of charge transfer in K<sub>3</sub>Cu to be more than  $1.4 \text{ e}^-/\text{Cu}$ . This means that the Cu atoms have fully filled 3*d* and 4*s* orbitals, corresponding to highly localized 3*d* and 4*s* bands [Fig. 3(d)]. The ionic interaction between K and Cu



FIG. 4. Fat-band structures for (a) K<sub>3</sub>Cu<sub>2</sub>, (b) K<sub>2</sub>Cu, (c) K<sub>5</sub>Cu<sub>2</sub>, and (d) K<sub>3</sub>Cu at 30 GPa. Thickness of the band represents the weight of contribution projected to atomic orbitals.

atoms is quantified by a small value of  $-ICOHP_{Cu-K}$  (0.489 eV/pair). An interesting feature of K<sub>3</sub>Cu is that the Fermi level just falls in the pseudo valley, which shows a tendency of opening a bandgap and therefore stabilizing the structure.

In predicted Cu-K compounds, Cu atoms are best described as anions with the valence electronic configuration of  $4s^2 3d^{10}4p^n$  $(0 < n \le 2)$ . To probe the oxidation state of Cu, we construct a series of model systems ( $\square_3 Zn_2$  and  $\square_3 Ga_2$  for K<sub>3</sub>Cu<sub>2</sub>,  $\square_2 Ga$  and  $\square_2$ Ge for K<sub>2</sub>Cu,  $\square_5$ Ga<sub>2</sub> and  $\square_5$ Ge<sub>2</sub> for K<sub>5</sub>Cu<sub>2</sub>, and  $\square_3$ Ga and  $\square_3$ Ge for K<sub>3</sub>Cu) by removing all K atoms in the lattice and replacing Cu with Zn/Ga/Ge. As illustrated in Fig. S6, the partial density of state (PDOS) profile of Cu-4p states in K<sub>3</sub>Cu<sub>2</sub> resembles more to the Ga 4*p* states in  $\Box_3$ Ga<sub>2</sub> rather than Zn 4*p* states in  $\Box_3$ Zn<sub>2</sub>, giving an evidence that the oxidation state of Cu in K<sub>3</sub>Cu<sub>2</sub> is -1.5 rather than -1. As a consequence, the electronic configuration for K<sub>3</sub>Cu<sub>2</sub> is described as  $(K^+)_3$  [Cu-Cu]<sup>3-</sup>. The neighboring Cu-Cu atoms in the linear chain are connected together with  $\sigma$  bonding by *sp* hybridization with the electronic configuration of  $4s^{1}4p_{z}^{1}$ , and the additional electron is partially filled in the 4  $p_x/p_y$  orbital and delocalized in the copper chains, forming multicenter  $\Pi_n^{n-}$  bonding. The charge density difference (CDD) map shown in Fig. 5 visualizes the electron accumulation around the linear Cu chains and the delocalization of  $\Pi_n^{n-}$  electrons. In particular, a high degree of electron accumulation can be observed at the center of neighboring copper atoms with a maximum value of 0.09 eV/Å<sup>3</sup>, corresponding to the *sp*-*sp* σ bonding.

For K<sub>2</sub>Cu, the PDOS profile of Cu 4p states is very close to that of the Ga 4*p* state in  $\Box_2$ Ga. Thus, the electronic configuration of  $4s^2 3d^{10} 4p^1$  can be assigned to the Cu atom corresponding to the anion. Consequently, distorted  $sp^2$  hybridization is adopted for Cu<sup>2</sup> Cu<sup>2–</sup> anions, where the electrons are distributed between neighboring Cu atoms, and in the remaining  $sp^2$  orbitals accommodating the zigzag chains. As shown in Fig. 5, the maximum CDD value  $(0.06 \text{ eV/Å}^3)$  is located in the midway between Cu atoms in the zigzag chain, corresponding the geometry of  $\sigma$  bonding, whereas the secondary maximum  $(0.05 \text{ eV/Å}^3)$  is along the  $[0 \ 1 \ 0]$  or  $[0-1 \ 0]$ direction on the bc plane. Just like K<sub>2</sub>Cu, the Cu atoms in K<sub>5</sub>Cu<sub>2</sub> adopt the electronic configuration of  $4s^2 3d^{10}4p^1$  as well, which corresponds to the dimeric [Cu–Cu]<sup>4–</sup> Zintl anion and also similar to the bonding situation of Au<sub>2</sub> in Ca<sub>5</sub>Au<sub>4</sub><sup>9</sup> and Ag<sub>2</sub> in Yb<sub>3</sub>Ag<sub>2</sub><sup>60</sup>. The Cu<sub>2</sub> dimer features  $\sigma$  type bonding by  $p_{\sigma}$ - $p_{\sigma}$  interaction between 4porbitals, revealed in the CCD contour (Fig. 5). For K<sub>3</sub>Cu, the PDOS profile of Cu 4*p* states is similar to that of the Ge 4*p* state in□<sub>3</sub>Ge, implying an -3 oxidation state for Cu with the  $4s^2 3d^{10} 4p^2$  configuration. The additional outer 4p electrons are less bound, which is confirmed by the 3D contour plot of the difference charge density. As shown in Fig. 5(d), the isolated  $Cu^{3-}$  anions are situated in the K cages with an isosurface of 0.03 e<sup>-</sup>/Å<sup>3</sup>. The density extremum outside the nuclei is about 0.05 eV/Å<sup>3</sup>, appearing at the longest separation of K-Cu along the [001] direction in CuK<sub>14</sub> polyhedra. This electron accumulation pattern behaves somewhat like electrides.<sup>61,62</sup> However, the separation from the electronic accumulation center



FIG. 5. Three dimensional charge density difference isosurface with the isovalue of 0.03  $e^{-/\hat{A}^3}$  for (a)  $K_3Cu_2$ , (b)  $K_2Cu$ , (c)  $K_5Cu_2$ , and (d)  $K_3Cu$  at 30 GPa. Corresponding 2D charge density difference maps are shown on the bottom. Cu and K are colored red and green, respectively.

to the copper anions is 1.22 Å, significantly shorter than that to the K cations (2.37 Å). Therefore, the accumulated electrons should be assigned to the Cu 4p electrons in the outer shell rather than electrides. In addition to the electron accumulation around the copper atoms, a large electron depletion can also be observed in the K framework, revealing the transfer of electrons from K to Cu atoms.

Our predicted K-Cu structures and analysis of the electronic structures show that copper can exist as a Zintl anion in compounds with the electronic configuration of  $4s^2 3d^{10}4p^n$ , taking advantage of electrons transferred from potassium. The Cu-Cu bonds are formed with single nature and primarily by the  $p_{\sigma}-p_{\sigma}$  interaction between the 4p orbitals of Cu. The degree of electron sharing in Cu-Cu bonds may be adjusted by modifying the potassium composition in the crystal. Going from K<sub>3</sub>Cu<sub>2</sub> to K<sub>3</sub>Cu, the bonding order decreases and the Cu species aggregates into linear chains, zigzag chains, Cu<sub>2</sub> dimers to isolated Cu anions. By alloying with electropositive metals, Cu has the *d*-band fully filled below the Fermi level and thus behaves like a *p*-block element. Application of Miedema's rules<sup>63</sup> to the formation of intermetallic compounds indicates that the two metals must have large difference in electronegativity and a small difference in charge densities at the Wigner-Seitz radius. These conditions are met under extreme pressure where the charge densities of both Cu and K are dramatically changed, allowing the compounds to form. The prediction of various Cu-K compounds is an illustration of new chemistry that occurs under high pressure, which can be readily tested by diamond anvil cell experiments.

#### CONCLUSIONS

In summary, extensive structure searches were carried out in K-Cu configuration space to search for stable crystal structures. Four K-Cu phases, namely, K<sub>3</sub>Cu<sub>2</sub>, K<sub>2</sub>Cu, K<sub>5</sub>Cu<sub>2</sub>, and K<sub>3</sub>Cu, are predicted for the first time to be thermodynamically stable within a moderate pressure range. Among the predicted structures, K<sub>3</sub>Cu<sub>2</sub> is identified as one structure of previously synthesized K-Cu compounds. The stimulated XRD pattern for K<sub>3</sub>Cu<sub>2</sub> agrees well with the experimental one, and the calculated range of stability (8.5-32 GPa) is consistent with the synthesis condition. In all predicted K-Cu phases, Cu atoms are situated in the hexagonal K sublattice with different dimensions, from isolated Cu atoms and Cu<sub>2</sub> dimers (0D) to infinite linear and zigzag chains (1D). Electronic structure analysis unveils that Cu in these compounds is anionized, thus acting as a *p*-block element with the electronic configuration of  $4s^2 3d^{10} 4p^n$  (0 < n  $\leq$  2). Strong Cu–Cu covalent interactions are found by *sp* hybridization for linear Cu chains in K<sub>3</sub>Cu<sub>2</sub>, by distorted *sp*<sup>2</sup> hybridization for zigzag chains in K<sub>2</sub>Cu, and by  $p-p \sigma$  bonding Cu<sub>2</sub> dimers in K5Cu2. The electron transfer from K to Cu plays an important role in the structural stability and induces ionic interaction in the crystal. Our results provide a deep insight into the understanding of the novel structure and properties of K-Cu compounds and stimulate future experimental investigations in this system.

#### SUPPLEMENTARY MATERIAL

The supplementary material contains calculated properties for predicted Cu–K compounds, including lattice parameters, atomic positions, elastic constants, enthalpies, phase diagram, phonon dispersion relations, x-ray diffraction patterns, and density of state, as well as visualization of crystal structures.

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#### DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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<sup>53</sup>Because the four K–Cu phases were predicated to be stable at 30 GPa, all of the bondlengths and electronic structures hereafter were calculated at 30 GPa unless otherwise stated.

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