

Electron Doping of Proposed Kagome Quantum Spin Liquid Produces Localized States in the Band Gap

Qihang Liu,^{1,2,*} Qiushi Yao,² Z. A. Kelly,³ C. M. Pasco,³ T. M. McQueen,^{3,4} S. Lany,⁵ and Alex Zunger^{1,†}

¹Department of Materials Science and Engineering, University of Colorado Boulder, Boulder, Colorado 80309, USA
²Department of Physics, University of Colorado Boulder, Boulder, Colorado 80309, USA
³Department of Physics, University of Colorado Boulder, Boulder, Colorado 80309, USA
⁴Department of Physics, University of Colorado Boulder, Boulder, Colorado 80309, USA
⁵Department of Physics, University of Colorado Boulder, Boulder, Colorado 80309, USA

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Carrier doping of quantum spin liquids is a long-proposed route to the emergence of high-temperature superconductivity. Electrochemical intercalation in kagome hydroxyl halide materials shows that samples remain insulating across a wide range of electron counts. Here we demonstrate through first-principles density-functional calculations, corrected for self-interaction, the mechanism by which electrons remain localized in various Zn-Cu hydroxyl halides, independent of the chemical identity of the dopant—the formation of polaronic states with attendant lattice displacements and a dramatic narrowing of bandwidth upon electron addition. The same theoretical method applied to electron doping in cuprate Nd_2CuO_4

order. Indeed, this is in-line with diverse types of materials that localize incoming electrons [45], suggesting that such description for added carriers is generally appropriate and needs not be specialized to QSL phases. A unit cell contains two Cu kagome layers with AA stacking, i.e., six Cu atoms.

method is introducing a potential operator that acts only on the doping states to restore the generalized Koopmans condition (see Supplemental Material for details of the DFT + U potential and the nonlocal external potential [29]). Here we apply both methods on kagome Zn-Cu hydroxyl halides for the cross validation of electron polaron formation.

To reach the generality of the electron-doping behavior of Cu^{2+} hydroxyl halides, we consider a variety of experimentally observed structures of $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{BrF}$. The first synthesized report suggested a $\text{P6}_3=\text{mmc}$ structure with Zn substitution widely ranging from $x = 0$ to 1 [6,42,43], while some of the authors reported an orthorhombic Cmcm structure with x less than 0.5 [44]. DFT local optimization is performed on all these input structures before calculating the electronic structures.

—As a representative, we first consider $\text{ZnCu}_3(\text{OH})_6\text{BrF}$ with a $\text{P6}_3=\text{mmc}$ crystal structure, as shown in Fig. 1(a). For simplicity, we assume a ferromagnetic alignment within each Cu kagome layer and an antiferromagnetic ordering between the neighboring Cu layers. The exchange interaction and doping effects of other magnetic configurations are summarized in the Supplemental Material [29]. From the calculations, we find that the response of the material to an added electron by localizing it does not depend on the details of the spin

electron potential λ_e is large enough (exceeds a critical value $\lambda_{cr} \sim 1.3$ eV) [29], we can stabilize the structure with local symmetry breaking, and the electron polaron forms, as shown in Figs. 2(b) and 2(d). The results of the Cu^{1+} polaron are qualitatively similar with the calculations using a hybrid functional, pertaining to the main feature of the d^9 - d^{10} transition inside the gap, as well as the doped electron localized at the $d_{x^2-y^2}$ orbital of one Cu^{1+} ion.

Figure 3(a) shows the evolution of structural and magnetic properties around a Cu ion in $\text{ZnCu}_3(\text{OH})_6\text{BrF}$ as a function of λ_e . It is apparent that during the d^9 - d^{10} transition, the Cu–O bond length increases and the local magnetic moment quenches. An appropriate choice of λ_e should fulfill the generalized Koopmans condition (1). Figure 3(b) shows the non-Koopmans energy Δ_{nk} , defined as $E(N) - E(N - 1) - \text{eig}(N)$, as a function of λ_e . We find that Eq. (1) is fulfilled at $\lambda_{lin} \sim 1.95$ eV, at which point the linearity is correctly recovered. Since we have $\lambda_{lin} > \lambda_{cr}$, the polaronic state with local symmetry breaking is physically meaningful in presenting the electron doping of $\text{ZnCu}_3(\text{OH})_6\text{BrF}$.

We next consider another spin-1=2 kagome antiferromagnet, i.e., $\text{Cu}_4(\text{OH})_6\text{BrF}$ (barlowite), which has also been proposed as a QSL candidate [3,43]bee4092Tj/86224a85,8H

To summarize, here we demonstrate the mechanism of insulating behaviors upon a wide range of electron doping in various Zn-Cu hydroxyl halides; i.e., the Cu-O manifold has an intrinsic tendency to localize added electrons into a self-trapped polaronic state. Such an electron-localization mechanism happens even without the disorder from chemical doping, standing as an important insight independent of any experiment. The doping-induced disorder, either by the randomness of the incoming carrier or the local distortion by the chemical dopant, may help further stabilize the polaron. Therefore, it is unlikely that

exact exchange-correlation energy functional and its functional derivative are known. Building on the central fact that DFT is an exact formal theory for the ground-state properties for the exact exchange-correlation energy functional, there is no reason why the properties noted above could not be captured by DFT in principle. In fact, many previously considered “classical correlated solids” have been recently treated by DFT with results that are fully consistent with experiment. For example, the existence of gaps and doping effects in “Mott insulators,” such as transition-metal oxides [53–56], or La_2CuO_4 [57], both thought for a long time to require heavy artillery of more advanced techniques, now appear to be described reasonably well by appropriately executed DFT. Whereas the exact ultimate functional is still unavailable, the current Letter represents the state of the art in DFT-doping calculations [9] by correcting the leading deficiency of previous DFT-doping applications via imposing the generalized Koopmans theory. Thus, we believe that it can predict the real physics without further over- or underestimation of the localization tendency. In addition, we note that the state of magnetic ordering can alter the band dispersions and thereby affect the localization energy, but does not in principle affect the localization mechanism. Although beyond the scope of this Letter, our approach is well suited for studying the interplay between magnetic order (or disorder) and electron localization, while fully accounting for spatial spin correlations. The spin liquid phase is expected to enhance the self-trapping localization effect because of the global spin disorder.

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