Tuning Topological Edge States of Bi(111) Bilayer Film by Edge Adsorption

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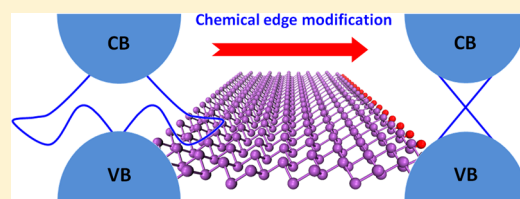
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S Supporting Information

ABSTRACT: Based on first-principles and tight-binding calculations, we report that the topological edge states of zigzag Bi(111) nanoribbon can be significantly tuned by H edge adsorption. The Fermi velocity is increased by 1 order of magnitude, as the Dirac point is moved from the Brillouin zone boundary to the Brillouin zone center, and the real-space distribution of Dirac states are made twice more delocalized. These intriguing changes are explained by an orbital filtering effect of edge H atoms, which pushes certain components of the p orbital of edge Bi atoms out of the band gap regime that reshapes the topological edge states. In addition, the spin texture of the Dirac states is also modified, which is described by introducing an effective Hamiltonian. Our findings not only are of fundamental interest but also have practical implications in potential applications of topological insulators.

KEYWORDS: 2D topological insulator, Dirac cone state, chemical edge modification, spin texture

S tudies of chemical and structural edge modification of two-dimensional (2D) materials are of great scientific and technological interest because such edge modifications are expected to significantly change the properties of 2D structures, especially 2D nanostructures because of a large edge-to-surface ratio, in analogy to the surface modification of 3D nanostructures with a large surface-to-volume ratio. One well-studied example is graphene nanoribbons (GNRs).[1−4] However, much less attention has been paid to edge modification of 2D topological insulators (TIs). This is because the topological nature of TI edge states, with a origin from bulk band topology, is well-known to be robust, insensitive to nonmagnetic chemical and structural edge modification.[5,6] Especially, some fundamental topology-defined properties of the TI edge state, such as its quantized edge conductance and spin-momentum locking relation, cannot be changed. On the other hand, other characteristic properties of TI edge states, such as carrier mobility, the number of quantum conductances, and the spin texture, can all in principle be changed by edge modification, but modification of the TI edge state has been rarely demonstrated.

Ultrathin Bi(111) films are theoretically predicted to be a 2D TI material,[7−11] which have been experimentally synthesized and characterized recently.[12−15] In this Letter, we demonstrate that the TI edge states in zigzag Bi(111) nanoribbon (ZBNR) can be tuned by chemical edge modification via H adsorption. Most remarkably, the Fermi velocity of Dirac edge state is increased by as much as 1 order of magnitude, when the Dirac

point is moved from the Brillouin zone boundary to Brillouin zone center. Correspondingly, the real-space distribution of Dirac states is found to be much more delocalized. In addition, the spin texture of the Dirac states is also modified, with the spin orientation switching from predominantly in-plane to out-of-plane alignment around the Dirac point. Through a systematic analysis based on model first-principles and tight-binding (TB) calculations, the physical mechanism underlying these intriguing phenomena is revealed to be the atomic orbital filtering effect by edge H atoms. The edge H pushes part of x- and z-components of p orbitals of the edge Bi atoms out of the band gap regime, leading to a change of edge boundary potential that reshapes the topological edge states. The change of spin texture is further analyzed by an effective Hamiltonian.

The first-principles calculations of ZBNR, containing 80 Bi atoms, including spin−orbit coupling and without/with H adsorption are carried out in the framework of generalized gradient approximation with Perdew−Burke−Ernzerhof functional using the VASP package.[16] The supercells have a vacuum layer more than 15 Å thick to ensure decoupling between neighboring ZBNRs. All self-consistent calculations are performed with a plane-wave cutoff of 400 eV on a 1 × 11 × 1 Monkhorst-pack k-point mesh. For structural relaxation, all of the atoms are allowed to relax until atomic forces are smaller

than 0.01 eV/Å. The TB calculations of ZBNR are done using the Wannier90 package.[17] First, the TB Hamiltonian of one unit cell, containing two Bi atoms and 12 maximally localized Wannier functions (MLWFs) of p orbitals, is fitted to the first-principles calculations. Using this unit-cell TB Hamiltonian, we further constructed a supercell TB Hamiltonian of ZBNR, containing 80 Bi atoms. To model the H adsorption effect, p orbitals of edge Bi atoms are selectively pushed out of the band gap regime in the TB calculations.

Figure 1a and b shows the first-principles band structures of ZBNR without and with edge H adsorption, respectively,
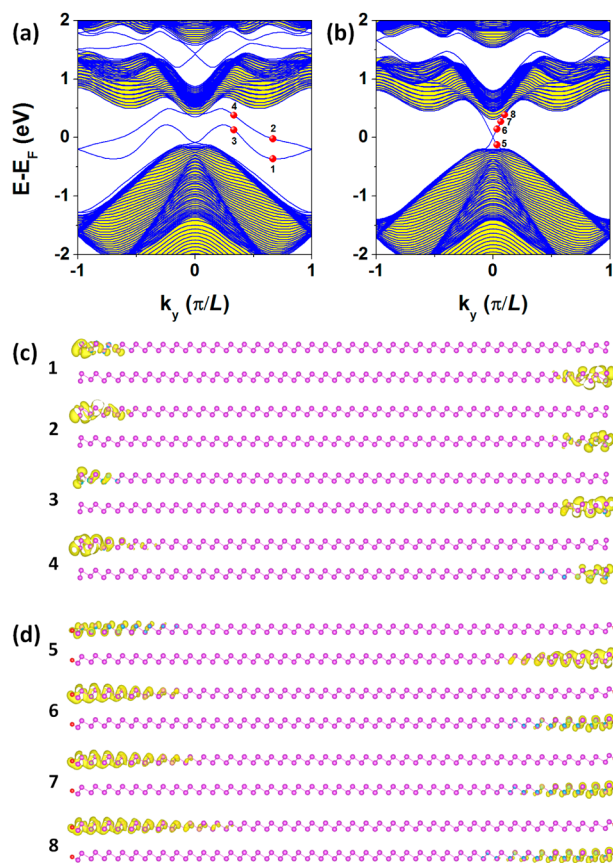

Figure 1. (a and b) First-principles band structures of ZBNR without and with edge H adsorption, respectively. The shaded yellow regions are bulk states with a band gap; the solid blue lines inside the band gap are topological edge states. (c and d) Side view of real-space charge density distributions of the edge states at different k-points, as marked in a and b, respectively.

illustrating the remarkably different topological edge states under different chemical edge environments. Without H adsorption (Figure 1a), there are two extended gapless edge states inside the bulk band gap. The two edge states, connecting the valence and conduction bulk bands (shaded yellow regions) and forming a 1D Dirac state at the Brillouin zone boundary, are characterized by an odd number of crossings over the Fermi level (from $k_y = 0$ to $k_y = 1$). Tuning the Fermi level within the band gap, the number of crossings can be either three or one, indicating the topological nature of ZBNR. Due to the inversion symmetry, each edge state is degenerated for the left and right edges. The real-space distribution of these degenerated edge states at four chosen k-points (as marked in Figure 1a) are shown in Figure 1c. We see that the width of

localized edge state is k-point dependent and its maximum width is ~2 nm, which is consistent with previous scanning tunneling microscopy (STM) measurement.[13]

However, with H adsorption at the edge of ZBNR, the topological edge states are dramatically modified in three important ways, as shown in Figure 1b and d. First, the most significant finding is that the Fermi velocity (v_F) of Dirac states, as obviously reflected by the band slope, is increased by as much as 1 order of magnitude, changing from 1.1×10^5 m/s to 0.9×10^6 m/s. This high Fermi velocity is comparable to the largest v_F (3×10^6 m/s) obtained from suspended graphene.[18] The Fermi velocity is one of the key parameters in the study of Dirac materials, as it bears various fundamental information, such as electron mobility, electron–electron interaction,[18] and effective fine structure constant.[19] Several different routes have been proposed to engineer v_F in graphene,[20] but few have been reported in TIs. Here, we demonstrate that chemical edge modification presents a simple and powerful way to engineer v_F in 2D TIs.

Second, the original extended gapless edge states become localized at Brillouin zone center in the k-space, similar to the edge states in HgTe/CdTe quantum well.[8] Consequently, there is only one crossing point between the edge state and Fermi level within the energy window of bulk band gap. This modification can have useful implications in spintronic devices. With one crossing, electron backscattering is in principle completely forbidden. Having three crossing points of the edge state and Fermi level, electron backscattering can no longer be 100% prohibited in a scattering process between two states with same energy but different momenta. This is because the spin directions of those two states are not completely inverse with each other.[13] Either three bands or one band in band gap will not change the topological properties of the ZBNR, as long as it is an odd number. The only difference is either six or two quantized conductances will be observed in the transport measurement.

Third, the real-space distribution of the localized edge states becomes much wider than those without H adsorption, as seen by comparing Figure 1d with Figure 1c. As the k-point moves away from the Dirac point, the localized edge states become more and more delocalized, whose width of distribution increases to a maximum of ~4.4 nm. This observation is consistent with the previous theory of penetration depth of edge states, which is inverse to k-space distribution of the edge states.[8] A localized state in momentum space will have an extended distribution in real space.

The results shown in Figure 1 demonstrate the feasibility of tuning some important characteristic properties of 2D TI edge states by chemical edge modification. Next, we perform an orbital analysis to reveal the physical mechanism underlying this phenomenon. There are one s orbital for each H atom and three p orbitals for each Bi atom, as schematically shown in Figure 2a. At the ribbon edge, each Bi atom is bonded with a H atom. Structural optimization confirms that the H–Bi bond is within the $z–x$ plane; i.e., it is perpendicular to the p_y, but not perpendicular to the p_x or p_z orbital of the Bi atom. Considering the orbital symmetry, it is easy to see that the hopping between s orbital of H and p_y orbital of Bi is zero, but the hopping between the s orbital of H and p_x (or p_z) orbital of Bi is not zero. Therefore, the effect of H atoms is to partially saturate p_x and p_z orbitals of edge Bi atoms.

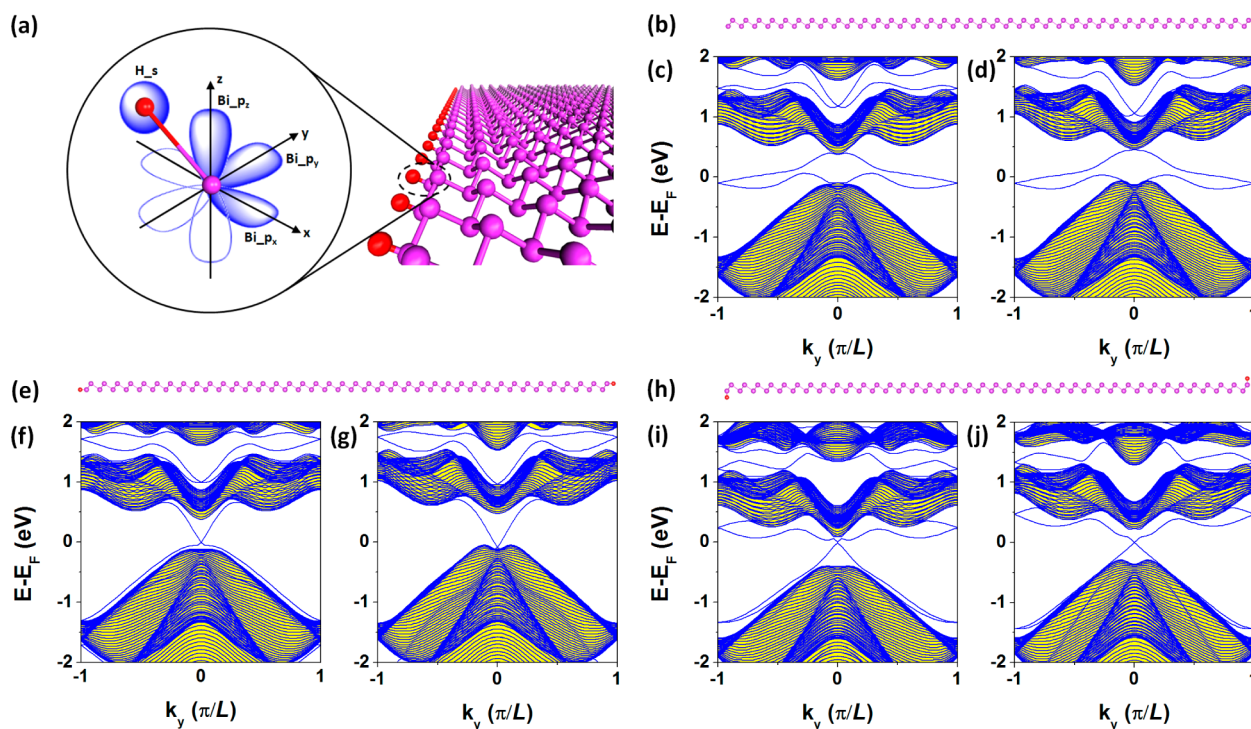To support such a hypothesis, we have further performed several first-principles and TB model calculations. First, we

Figure 2. (a) Illustration of the orbital and bonding at the edge of ZBNR with H adsorption. One s orbital for each H atom and three p orbitals for each Bi atom are shown. (b, e, and h) Atomic structures of ZBNR without H adsorption, with H adsorption along the x-direction, and with H adsorption along the z-direction, respectively. The atomic structures are not relaxed. (c, f, and i) First-principles band structures of b, e, and h, respectively. (d, g, and j) TB band structures of b, e, and h, respectively.

construct a TB Hamiltonian of ZBNR using the ideally bulk-terminated edge without edge structural relaxation (Figure 2b). The band structures obtained from the first-principles and TB model calculations are shown in Figure 2c and d, respectively. We see good agreement between the two methods for both bulk and edge states, validating the effective TB Hamiltonian. Next, we artificially fix the adsorbed H atoms along either x- or z-direction without structural relaxation, while maintaining the inversion symmetry of the ribbon, as shown in Figure 2e and h, respectively. This special setup allows us to selectively saturate either p_x or p_z orbital of the edge Bi atoms. Thus, we can distinguish the effect of those two orbitals from each other. The H−Bi bond length is set to 1.82 Å, as obtained from the relaxed structure in Figure 1d.

The first-principles band structures for the above two different H-adsorbed model configurations are shown in Figure 2f and i, respectively. The most significant finding is that a new Dirac state appears at Brillouin zone center in both cases. In the x-direction H-adsorbed configuration when the p_x orbital of edge Bi atoms is pushed out of the band gap regime (Figure 2f), the upper branch of the new Dirac state spans the whole energy window of the bulk band gap, while the lower branch of the new Dirac state almost merges into the bulk valence bands. However, in the z-direction H-adsorbed configuration when the p_z orbital of edge Bi atoms is pushed out of the band gap regime (Figure 2i), the lower branch of the new Dirac state spans the most energy window of bulk band gap. Both upper and lower branches of the new Dirac state have an extended dispersion, resulting in two additional Dirac states at the Brillouin zone boundary.

To more clearly see the H adsorption effect in above two configurations, we also selectively pushed the p_x or p_z orbitals of edge Bi atoms out of the band gap regime in the TB

Hamiltonian. This can be done by adding a large on-site energy on these selected orbitals, similar to a method used previously to study the gapless edge state in GNR.[21] The corresponding TB band structures are shown in Figure 2g and j for pushing p_x and p_z orbital, respectively, which are consistent with the first-principles results of Figure 2f and i. The comparison between the first-principles and TB calculations indicates that the H atoms act as an orbital filter,[11] which selectively pushes the orbital of edge Bi atoms and reshape the topological edge states. It is the combined effect of partial pushing of both p_x and p_z orbitals of edge Bi atoms out of the band gap regime that is responsible for generating the new gapless Dirac edge states in Figure 1b by H edge adsorption.

It is interesting to note that if both p_x and p_z orbitals of edge Bi atoms were completely pushed out of the band gap regime simultaneously, e.g., by adsorbing two H atoms on the edge Bi atoms, the Dirac state would remain located at the Brillouin zone boundary, as shown in Figure 3a. Also, the effect of pushing the p_y orbital of edge Bi atoms has been studied. It would reshape the edge states and induce two Dirac states at Brillouin zone boundary, as shown in Figure 3b. However, practically it is hard to find a way to just push the p_y orbital. Furthermore, if there is no chemical adsorption, structural relaxation alone will not change the position of Dirac point and hence without significantly changing the shape of edge state. This can be seen by comparing the first-principles band structures of ZBNR with (Figure 1a) and without (Figure 2c) structural relaxation.

Next, we explain where the new gapless Dirac edge state at Brillouin zone center comes from. The TB model provides us with an easy method to analyze the evolution of topological edge states upon edge modification. We can continuously push p_x and p_z orbitals of edge Bi atoms by increasing their on-site
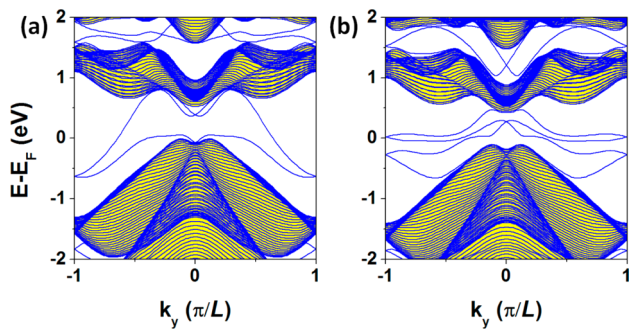
Figure 3. (a) The TB band structure of ZBNR by completely pushing both the p_x and p_z orbitals of edge Bi atoms out of the band gap regime. (b) The TB band structure of ZBNR by completely pushing the p_y orbital of edge Bi atoms out of the band gap regime.

energies gradually in the TB Hamiltonian. As shown in Figure 4a−c, by gradually increasing the on-site energy of p_x orbital, the edge states are continuously reshaped. The upper branch of the old Dirac state merges into the conduction bands, and the lower branch of the old Dirac state becomes the upper branch of the new Dirac state, locating the Dirac point at Brillouin zone center. However, the case for p_z orbital is a little different, as shown in Figure 4d−f. By gradually increasing the on-site
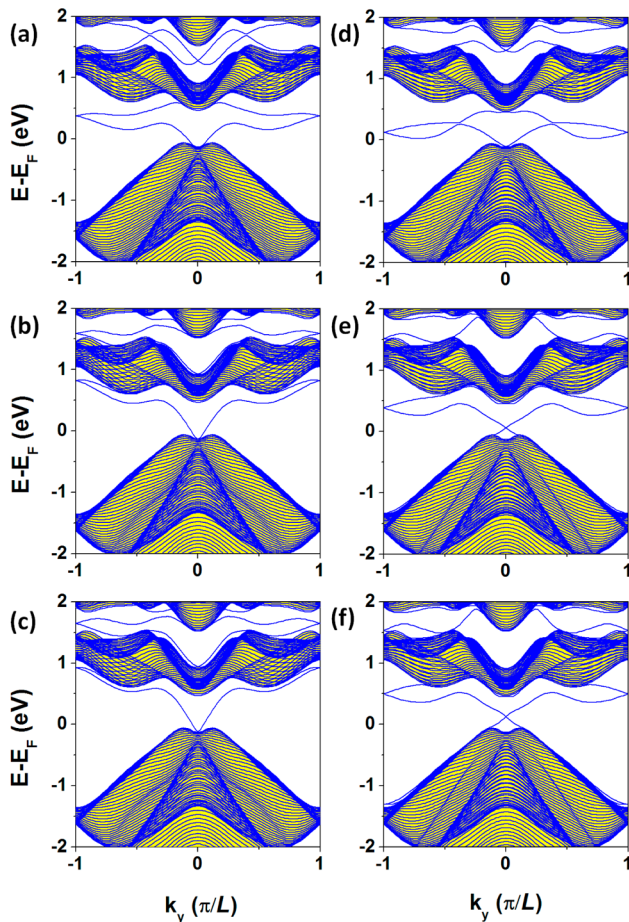

Figure 4. (a−c) Evolution of the topological edge states by gradually pushing p_x orbital of the edge Bi atoms. (d−f) Evolution of the topological edge states by gradually pushing the p_z orbital of the edge Bi atoms. From (a−c) and (d−f), the on-site energy for p_x and p_z orbitals are set at 1, 3, and 5 eV, respectively.

energy of p_z orbital, the edge states are continuously moved upward. Part of the old Dirac state merges into the conduction bands, and the new Dirac state is pulled up from the valence bands. The bulk states are not changed in both cases. From this model calculation, we found that, depending on the edge potential, the topological edge states can be either regenerated from or merged into the bulk states, always being connected to bulk states.

Lastly, we show that the spin textures of topological edge states can also be modified by chemical edge modification. The zoom-in first-principles band structures and spin textures around the Dirac states without and with H adsorption are shown in Figure 5a and b, respectively. We see that the spins
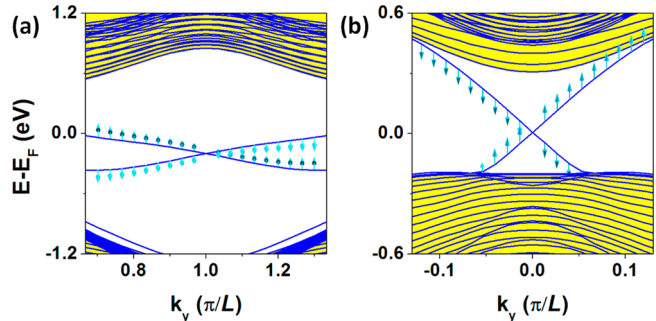

Figure 5. (a and b) Zoom-in band structures around the Dirac point for Figure 1a and b, respectively. The arrows, perpendicular to momentum, denote the spin textures of edge states. Only the left edge-state spin textures are plotted for each band, which are inverse to the right edge-state spin textures.

are within the $z−x$ plane and perpendicular to the momentum direction (y-direction), showing the helical nature and spin-momentum locking property. Without H adsorption (Figure 5a), the in-plane (x-direction) spin component is dominant near the Dirac point. When the k-point goes away from the Dirac point, the out-of-plane (z-direction) spin component becomes larger. With H adsorption (Figure 5b), the out-plane (z-direction) spin component is dominant near the Dirac point. When the k-point goes away from the Dirac point, a small in-plane (x-direction) spin component starts to appear. Thus, the spin direction is wrapping along the Dirac state with different momenta in the two cases. Such a spin texture of the 1D Dirac states can be described by the following low-energy effective Hamiltonian,

$$H = s\hbar\nu_F k_y [\lambda(k_y)\sigma_x + \sqrt{1 - \lambda^2(k_y)}\,\sigma_z] \qquad (1)$$

where $s = \pm 1$ denotes the right/left edge, ν_F is the Fermi velocity, and $\sigma_{x/z}$ is the pauli matrix. $\lambda \in [-1,1]$; it is a wrapping function of momentum k_y. If $\lambda = 0$, the spin only has a z-component. If $\lambda = \pm 1$, the spin only has an x-component. In other cases, the spin can have both x- and z-components, and spin direction is tuned by the value of λ.

Our theoretically predicted chemical edge modification of the topological edge state is based on the calculation of a free-standing Bi film. However, similar to the case of graphene, it is generally difficult to obtain a free-standing Bi film with perfect edge orientation in experiment. On the other hand, recent experimental work has shown the possibility of growing Bi film on a TI substrate with very good edges and detectable topological edge state.[13] We expect that our prediction of modified edge properties can be also detected for Bi film grown

on a substrate. To this regard, the effects of substrate and edge roughness should be further studied in the future.

In conclusion, although the topology of TI edge states is robust against structural and chemical edge modification, we show that some important characteristic properties of TI edge states can still be significantly modified, as illustrated by H edge adsorption in ZBNR. Most remarkably, the Fermi velocity can be increased by as much as 1 order of magnitude, becoming comparable to the largest value found in graphene. Also, the spin textures of TI edge states are modified. Our findings are scientifically interesting for a better understanding of basic properties of topological edge states in relation to edge boundary conditions, in addition to bulk topology. They also have significant practical implications, because those modified properties, such as Fermi velocity and spin texture, are important parameters in TI-based spintronic devices. The approach of engineering topological edge states by chemical edge modification is general, not only applicable to other 2D TIs but can also be extended to 3D TIs via chemical surface modification.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Low-energy effective Hamiltonian and the corresponding spin textures for the 1D Dirac state. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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