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## Peculiar bond characters of fivefold coordinated octet compound crystals†

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The present work exemplifies complementary perspectives offered by the band and bond pictures of solids, with an emphasis on the chemical intuition pertaining to the latter, especially in the presence of interfaces. The modern computational method of constructing a unique set of maximally localized Wannier functions from delocalized band states imparts new interpretations to the familiar concept of chemical bonds in the context of crystalline solids. By bridging the band and bond pictures using advanced computational tools, we reveal for the first time the unusual bond characters of a long-predicted fivefold coordinated structure of binary octet compounds  $A^N B^{8-N}$  consisting of  $AA'$  stacked planar AB honeycombs. While the isolated monolayer retains the familiar  $p_z$ - $\pi$  bonding in a honeycomb framework as in graphene and hexagonal boron nitride, the bulk foregoes in-plane  $\pi$  bonding and embraces out-of-plane  $\cdots A-B-A-B \cdots$  chain bonding *via* overlapping  $p_z$  orbitals. Not only does the chemical intuition gained by invoking the bond picture clarify the chemical nature of the fivefold coordination, but it also facily explains a salient discrepancy in theoretical predictions in otherwise sound ample experimental evidence in the form of epitaxial thin films, paving the way towards rational synthesis of such thin films for optoelectronic applications. On the other hand, we show that the conduction band minimum, important in determining the electrical and optical properties, is a distinctly extended state that can only be properly described within the band picture.

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## Introduction

The band and bond pictures of solids offer complementary perspectives, with the latter conducive to chemical intuition especially in the presence of interfaces and defects.<sup>1,2</sup> Chemical bond characters of a material, not apparent from the extended energy and momentum eigenstates in the band picture, can provide insight into the structure, properties, and synthesis of the material, as we shall show here for a fivefold coordinated phase of binary octet compounds  $A^N B^{8-N}$  consisting of  $AA'$  stacked planar AB honeycombs<sup>3-5</sup> (Fig. 1a and b).

Under ambient conditions, group IV-IV, III-V, and many II-VI binary octets exhibit fourfold coordinated polymorphs including zinc blende and wurtzite, as well as numerous stacking variations,<sup>6-8</sup> whereas higher ionicity compounds are stable in structures of higher coordination numbers (*e.g.* MgO

in the NaCl structure). Boron nitride is unique due to the  $sp^2$ -coordinated,  $AA'$ -stacked layered polymorph h-BN; it is so stable that it had been unclear whether h-BN or the zinc blende phase (z-BN) is the thermodynamically stable phase until z-BN was generally accepted as such.<sup>9</sup>

The fivefold coordinated structure is an intermediate predicted for some  $A^N B^{8-N}$  between phases characterized by coordination numbers  $N_c = 4$  and 6, along the paths of structural transitions exhibiting a general trend of increasing  $N_c$  with increasing ionicity upon successive compression.<sup>4,5,10-17</sup> This structure has the same symmetry ( $P6_3/mmc$ ) as h-BN and is referred to as the h-MgO structure (just as NaCl for the rocksalt structure, the compound not necessarily MgO) since it was first predicted for MgO<sup>4</sup> or as the 5-5 structure for the mutual fivefold coordination,<sup>5,16-19</sup> or simply as HX standing for hexagonal.<sup>11</sup> As the present work focuses on bonding, we emphasize that the h-MgO structure is distinct from that of h-BN, consisting of threefold coordinated layers held together by a weak van der Waals (vdW) interlayer interaction. A compilation of the literature reveals the overall trend as well as the positions of the h-BN ( $N_c = 3$ ) and h-MgO ( $N_c = 5$ ) structures along the paths (see the ESI† for details).

Previous theoretical studies addressed crystal and electronic structures,<sup>3-5</sup> whereas the characters of chemical bonds, especially the unusual bonds between the adjacent (0001) planes, are largely left unexplored, with fivefold coordination defined

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Fig. 2 Structural features of the h-MgO structure in contrast to those of h-BN. (a) Ratios of the interlayer distance ( $c_h/2$ ) to intralayer bond length ( $a_h/\sqrt{3}$ ). (b) Interlayer binding energies, defined as monolayer-to-bulk total energy difference per cation-anion pair. (c) Monolayer-to-bulk lattice parameter ratios ( $a_{1L}/a_h$ ).

spectra will guide the experimental verification of the synthesis of these materials. In EELS, the energy loss near-edge structure (ELNES), by replicating the density of unoccupied states,<sup>39,40</sup> reveals the electronic structure of unoccupied states thus providing reliable information on bonding and coordination.<sup>41</sup> As discussed in the ESI,<sup>†</sup> under the dipole approximation,<sup>42,43</sup> angle-resolved near-edge spectra are closely related to densities of states projected onto  $p_z$ - and  $p_{x,y}$ -like symmetries, whereby transition peaks are identified as originating from  $\pi^*$  ( $p_z$ ) and  $\sigma^*$  ( $p_{x,y}$ ) states.<sup>43–47</sup> For 2D and layered materials such as graphene, graphite, and h-BN, both angle-resolved ELNES and polarization-resolved XANES have experimentally revealed  $\pi^*$  and  $\sigma^*$  transitions, as predicted by density functional theory (DFT) calculations with core hole effects properly considered.<sup>44,47,48</sup> Fig. 3 shows calculated core-level transition spectra of h-AlN and h-MgO in comparison with those of h-BN, in which the  $p_z$  edges are lower in energy than the  $p_{x,y}$  ones, consistent with the familiar energy sequence<sup>1,38,49</sup> that  $\pi^*$  states are lower than  $\sigma^*$ . Both the  $p_z$ - and  $p_{x,y}$ -like spectra of bulk h-BN are very similar to their respective 1L counterparts, due to the weak vdW interlayer interaction. While 1L h-AlN and h-MgO share this energy sequence ( $p_{x,y}$  higher than  $p_z$ ), manifesting  $\sigma$  and  $\pi$  bond formation from  $sp^2$  and  $p_z$  orbitals, respectively, the bulks exhibit a reversed sequence, which, along with the longer in-



Fig. 3 Near K-edge fine structure core-level spectra of 1L and bulk hexagonal crystals: (a and b) bulk and 1L h-BN, (c and d) h-AlN, and (e and f) h-MgO. Transitions from the  $1s$  core orbitals to  $p_{x,y}$ - and  $p_z$ -projected unoccupied states are plotted separately. Energy is referenced to the lowest transition energy.

plane cation-anion bonds in bulks than in monolayers (Fig. 2c), indicates that the bonding in the nonlayered bulks must be altered from the familiar model of  $\sigma$  and  $\pi$  bonds for the corresponding monolayers.

The above strong indicators of interlayer bonding, along with the anomaly in core-level transition spectra, warrant an investigation into the chemical bond characters of the h-MgO structure. The in-plane  $120^\circ$  angle suggests  $sp^2$  coordination, which is verified by simulated transition spectra of 1L h-AlN and h-MgO. If the interlayer interaction in the bulk materials is essentially ionic, so should be the in-plane bonding since the bond length ratio is near unity. If, however, the  $120^\circ$  coordination originates from  $sp^2$ - $\sigma$  bonding rather than just due to inherited symmetry from the constituent monolayer, what bonds are formed by  $p_z$  orbitals? We answer these questions in the following sections by bridging the bond and band pictures of solids.

Fig. S2<sup>†</sup> displays the band structures of the monolayer and bulk of the h-MgO phase followed by those of the wurtzite phase, in each column, of compounds BN, AlN and MgO in the rows for comparison. While 1L h-BN, h-AlN, and h-MgO all exhibit similar valence band structures originating from





Fig. 4 Isosurface plots of  $p_z$  Wannier orbitals in (a–c) 1L and (d–f) bulk h-BN, h-AlN, and h-MgO, each showing the side view of one primitive unit cell, with colored spheres representing the atoms labeled at the bottom of the figure. For better visualization in structural context, the TOC graphic displays one N-centered Wannier isosurface in the 3D model for each of 1L and bulk h-AlN. All isosurfaces are at the same isovalue,  $\pm 0.15$  ( $\text{e} \text{ \AA}^{-3})^{1/2}$ , with signs indicated by red (+) and blue (–) colors.

threefold coordinated  $\sigma$  and  $\pi$  bonding, bulk h-AlN and h-MgO bear less resemblance in band structures to their monolayers, surprisingly, than to their wurtzite counterparts. In contrast to the layered material h-BN,<sup>50,51</sup> bulk h-AlN and h-MgO exhibit strong dispersion along  $\Gamma A$ ,  $HK$ , and  $ML$  in the  $c$  direction. Moreover, both bulk h-AlN and h-MgO exhibit wider valence band energy spans along each of these lines than their respective wurtzite counterparts, indicating a stronger interlayer interaction for the fivefold coordinated polymorph than for the fourfold.

To visualize the nature of chemical bonding with MLWFs,<sup>1</sup> Fig. 4 depicts symmetry-adapted,<sup>52</sup> anion-centered  $p_z$  Wannier orbitals of h-BN, h-AlN, and h-MgO, and Fig. 5 shows the in-plane bond-centered  $sp^2$  MLWFs simultaneously generated without symmetry adaption. For h-BN, the in-plane MLWFs indicate  $\sigma$  bonding *via*  $sp^2$  hybridization, consistent with that reported by Halo *et al.*<sup>53</sup> and reminiscent of graphene.<sup>1</sup> The  $sp^2$  Wannier orbitals of the 1L and the bulk look similar to each other and so do the  $p_z$  orbitals, visualizing a familiar picture,<sup>9</sup> where the  $\sigma$  bond forms *via*  $sp^2$  electron transfer from B to N whereas N atoms share  $p_z$  electrons with B to form  $\pi$  bonds, although the  $\sigma$  bond appears less covalent in bulk than in 1L h-BN. As ionicity increases from h-BN to h-AlN and then to h-MgO, the  $\sigma$  bond center shifts further towards the anion (Fig. 5), but the tendency for the anion to donate  $p_z$  electrons can still be seen for the isolated monolayers albeit lesser in 1L h-MgO (Fig. 4). While the familiar picture of  $\sigma$  and  $\pi$  bonding persists for the monolayers, bulk h-AlN and h-MgO display a drastically different picture: the  $p_z$  Wannier orbitals are almost rotationally symmetric, with the  $0.15$  ( $\text{e} \text{ \AA}^{-3})^{1/2}$  isosurfaces not protruding towards the cations but reaching the adjacent layers, indicating the absence of  $\pi$  bonding and manifesting interlayer electron orbital overlaps. The localized Wannier orbitals indicate in-plane  $\sigma$  bonding in the bulk h-MgO structures and suggest interlayer  $p_z$  electron sharing.

Projecting extended Bloch states, especially those near band extrema, onto atomic orbitals is another way to reveal chemical bonding characters. Fig. S3† displays densities of states projected onto cation- and anion-centered local orbitals with  $s$ ,  $p$ , and  $d$  characters (*i.e.* with angular momentum quantum numbers  $l = 0, 1$ , and  $2$ ) for h-BN and h-AlN in both 1L and bulk forms, alongside corresponding fat band plots. For both monolayers, the lower valence bands exhibit predominant  $s$  characters with minute  $p$  contributions, and the upper valence bands with a degenerate maximum at  $\Gamma$  are dominated by  $p$  states but mixed with  $s$  characters. To resolve the “missing  $\pi$ ” mystery of bulk h-MgO structures, Fig. 6 presents fat band plots with  $p$  states further resolved into  $p_{x,y}$  and  $p_z$  states for h-AlN, compared with h-BN. As expected, for both 1L h-BN and h-AlN, the valence bands that peak at K stem from  $p_z$  states while those with maxima at  $\Gamma$  originate from  $p_{x,y}$ , manifesting  $sp^2$  bonding. Upon the formation of bulk h-BN by stacking the monolayers, each valence band splits into two with a relatively narrow splitting. Each pair of split bands essentially exhibits the same sign of curvature, and all valence bands show minimal dispersion in the vertical direction ( $c^*$ , along  $\Gamma A$ ,  $KH$ , and  $ML$ ). The in-plane splitting and  $c^*$  direction dispersion are consistent with the weak interlayer interaction of h-BN.

For bulk h-AlN, with regard to the monolayer, the  $p_z$  valence band splits into two bands with opposite signs of curvature and a wide splitting of  $\sim 7$  eV at  $\Gamma$ , indicating strong interactions between  $p_z$  orbitals in neighboring atomic planes. The split  $p_{x,y}$  bands, on the other hand, exhibit the same sign of curvature (also the same as in 1L) and a smaller splitting of  $\sim 2$  eV at  $\Gamma$ , naturally following the smaller overlaps between  $p_{x,y}$  orbitals of neighboring layers. From these observations, emerge the bonding scheme of the fivefold coordinated h-MgO type structures of octet compounds  $A^N B^{8-N}$ , graphically illustrated for bulk h-AlN in Fig. 6. With the  $\sigma$  bond frameworks of constituent atomic planes intact, each anion B partially donates  $p_z$  electrons to cations A in neighboring layers, forming  $\cdots A-B-A-B \cdots$  cation–anion chains in the  $c$  direction. For the lower-energy  $p_z$  bonding states, the  $p_z$  orbitals of neighboring cations and anions are in phase and therefore this band exhibits the same curvature as the  $\pi$  bonding band in 1L h-AlN. Conversely, the higher energy  $p_z$  bonding band has neighboring  $p_z$  orbitals out of phase and accordingly an opposite curvature. The apparent shift of the VBM from K (for 1L h-AlN) towards  $\Gamma$  (for bulk h-AlN) is actually the splitting into multiple bands upon stacking of multiple layers, eventually resulting in the two  $p_z$  bonding bands in the bulk limit. The absence of  $\pi$  bonding naturally explains longer in-plane bonds in the bulk materials than in the corresponding isolated monolayers ( $a_{1L} < a_h$  in Fig. 2c).

In comparison with h-BN, where the AA' stacking is dictated by electrostatic forces but the interlayer distance is set by vdW forces,<sup>54</sup> for the fivefold coordinated h-MgO structures with increased ionicity, it is naturally understood that the stronger electrostatic interaction not only dictates the stacking and registration between neighboring honeycomb layers, but also forces interlayer distances to be smaller than those determined solely by vdW forces. In a gedanken process to assemble the bulk h-MgO structure from isolated monolayers, the  $p_z$  orbitals





Fig. 5 Isosurface plots of  $\sigma$  bond Wannier functions and Wannier electron charge densities of 1L and bulk h-BN, h-AlN, and h-MgO. All Wannier function isosurfaces are at the same isovalue,  $\pm 0.15$  ( $e \text{ \AA}^{-3})^{1/2}$ , with signs indicated by red (+) and blue (–) colors, and the charge density isovalue is  $0.0675 e \text{ \AA}^{-3}$  ( $= 0.15^2 \times 3 e \text{ \AA}^{-3}$ , exactly corresponding to the Wannier function isovalue, as total charge density of three  $\sigma$  bond Wannier orbitals is plotted). Colored spheres representing the atoms are labeled for clarity. These  $\sigma$  bond MLWFs are simultaneously generated with the  $p_z$  Wannier orbitals as shown in Fig. 4 but without symmetry (reflection with regard to the atomic plane) adaption.

of the anions will significantly overlap those of the cations in neighboring layers, rendering preferred interlayer  $p_z$  electron sharing over the usual intralayer sharing that results in  $\pi$  bonding in the monolayers (Fig. 6). Nevertheless, the transition from in-plane  $\pi$  bonding in h-BN to vertical  $p_z$  chain bonding in h-MgO structures of higher-ionicity  $A^N B^{8-N}$  is evolutionary rather than abrupt. We have found that h-BeO is the intermediate in between, which warrants separate investigations; this work focuses on the fivefold coordinated h-MgO type polymorphs that exhibit distinctive vertical  $p_z$  chain bonding.

We now examine the conduction bands of h-AlN, starting with the global conduction band minima (CBMs) of both the monolayer and bulk at  $\Gamma$ , around which the bands are parabolic and largely isotropic, even between the in-plane and vertical directions of the bulk. Furthermore, the CBMs exhibit virtually no p character and very low densities of states compared with higher empty band extrema. Bacaksiz *et al.*<sup>3</sup> refer to these states as free-electron-like surface states. Here, we mention in passing that these states are indeed reminiscent of the free-electron

states in graphene, graphite, and h-BN,<sup>55</sup> with discussions to follow after we examine the  $p_z$  and  $sp^2$  antibonding states at higher energies. The s,  $p_{x,y}$  and  $p_z$  projected weights (Fig. 6) reveal  $sp^2$  and  $p_z$  antibonding characters of those higher conduction bands. Going from 1L to bulk h-AlN, the 1L  $\sigma^*$  state around 12 eV at  $\Gamma$ , contributed by s and  $p_{x,y}$  projected states, splits by  $\sim 3$  eV, whereas the 1L  $\pi^*$  band largely splits into two  $p_z$  antibonding bands as indicated by double headed arrows in Fig. 6. Similar to the  $p_z$  bonding bands, the two widely split antibonding bands have opposite curvatures, attributable to a lower- and higher-energy configuration with in-phase and out-of-phase in-plane neighboring  $p_z$  orbitals, respectively (Fig. S4†). Not surprising, the antibonding bands span over large ranges of energy and exhibit significant mixing with one another and with the free-electron-like states.

By now we can bring a close to the “missing  $\pi$ ” mystery in the near-edge transition spectra of the h-MgO type crystals. The  $\pi$  bonding is indeed missing, giving way to interlayer  $p_z$  chain bonding. Going from 1L to bulk, the  $p_z$  bonding band maximum





Fig. 6 Fat band plots showing projected weights onto cation- and anion-centered  $s$ ,  $p_{x,y}$ , and  $p_z$  orbitals for 1L and bulk h-AlN (upper panel), compared with those of h-BN (lower panel). For h-AlN, band states with predominant  $\sigma$ ,  $\sigma^*$  and  $\pi$ ,  $\pi^*$  characters are labeled in the  $p_{x,y}$  and  $p_z$  plots, respectively. Going from 1L to bulk, the  $\pi$  band splits into two  $p_z$  bonding bands, and the  $\pi^*$  band can be largely considered to split into two  $p_z$  antibonding bands as indicated by the double headed arrows; the  $p_z$  antibonding bands exhibit considerable mixing with  $\sigma^*$  and free-electron-like bands. Bonding schemes derived from the projection are visualized on the right, where the  $\sigma$  bonds are depicted as thick black lines and the  $p_z$  orbitals as balloons with colors (red and blue) signifying orbital wavefunction signs, solid filling indicating filled orbitals, and each dot visualizing an electron.







the basal-plane lattice parameter to the monolayer ( $a_{1L} \approx a_w$ ). The insight into the limitations in previous experiments points to rational strategies for reliably synthesizing large-area thin films of h-MgO structured  $A^N B^{8-N}$  for potential optoelectronic applications, expected from more favorable properties entailed by their higher symmetry over the common wurtzite phase, as well as similar band structures (direct gap, GW-corrected gap value, etc.) to their widely used wurtzite counterparts. The application-favorable direct band gaps of the bulk fivefold coordinated  $A^N B^{8-N}$  crystals are in part due to the free electron-like “channel states”, which are more conveniently studied in the band picture that complements the bond picture.

## Conflicts of interest

There are no conflicts to declare.

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