New topological states of matter, topological crystalline insulators (TCIs) [11], have been identified that extend the topological classification beyond the prototypical $Z_2$ classification based on time reversal symmetry [24]. In TCIs, topological properties of electronic structure such as the presence of robust metallic surface states arise from crystal symmetries instead of time-reversal symmetries. There are many proposed TCI phases depending on different crystal symmetries [4, 9], yet those relying on mirror symmetry [10] are of particular interest because they have been experimentally observed in, for example, IV-VI semiconductors SnTe, Pb$_{1-x}$Sn$_x$Te, and Pb$_{1-x}$Sn$_x$Se [11–15]. More materials are theoretically proposed to realize the TCI phases such as rocksalt semiconductors [10, 17], pyrochlore iridates [18], graphene systems [19], heavy fermion compounds [20, 21], and antiperovskites [22], including two-dimensional (2D) materials such as SnTe thin films [23, 24] and a (001) monolayer of PbSe [25].

Mirror-symmetric TCIs are mathematically characterized by mirror Chern numbers (MCNs). The MCN is a topological invariant defined by $\mu_1 = (\mu_+ - \mu_-)/2$ where $\mu_+$ and $\mu_-$ are Chern numbers of Bloch states with the opposite eigenvalues of a mirror operator ($M_z$) calculated on the mirror-invariant plane at $k_z = 0$ in the Brillouin zone (BZ). In a three-dimensional (3D) crystal, there is a second MCN ($\mu_2$) defined on the mirror-invariant plane at the boundary of the BZ $k_z = \pi$ (in units of $1/\alpha$, where $\alpha$ is the length of the primitive lattice vector along the $z$-axis) [20]. Moreover, considering different mirror symmetries, multiple pairs of MCNs ($\mu_1, \mu_2$) can be simultaneously present in three dimensions. A complete characterization of 3D TCIs requires consideration of all the MCNs, which may allow for the possibility of new states of matter, where MCNs are locked together or undergo separate transitions. Nonetheless, previous study based only on $\mu_1$ has not explored this situation.

In this paper, by considering MCNs on all inequivalent mirror-symmetric planes in reciprocal space, we study new topological states of matter realized in a 3D layered crystal generated by stacking 2D TCI layers. We show that the layered system realizes a new class of 3D TCIs when inter-layer interaction is weak, which we will refer to as a layered TCI. The layered TCI is characterized by equal and nonzero first and second MCNs $\mu_1 = \mu_2 \neq 0$ with a number of metallic surface states equal to $|\mu_1| + |\mu_2|$. Increasing the inter-layer interaction, we then show that the layered TCI undergoes topological phase transitions that change the MCNs ($\mu_1, \mu_2$). Based on first-principles calculations, we predict that a heterostructure consisting of alternating layers of PbSe monolayer and hexagonal BN (h-BN) sheet realizes the layered TCI indexed by (2,2), and that it undergoes distinct topological phase transitions in the sequence ($\mu_1, \mu_2$): (2,2) $\rightarrow$ (0,2) $\rightarrow$ (0,0) under external uniaxial tensile strain. Our findings shed light on new states of matter allowed by the presence of multiple MCNs in a 3D crystal. They may also help guide the discovery of more topological materials.

Before presenting the results, we first briefly explain...
how 2D TCI layers with a non-zero MCN $\mu_{2D} = n$ ($n \neq 0$) can be stacked into a new class of 3D TCIs characterized by $\mu_1 = \mu_2 = n$. Consider first a layered system consisting of 2D TCIs with $\mu_{2D} = n \neq 0$ stacked along the normal direction to the plane (defined as z-direction) as shown in FIG. 1(a). The layered system then respects the mirror symmetry $M_z$ that defines the MCN of the 2D TCI $\mu_{2D}$ in the plane of each layer. Now, let us initially assume that the interaction between the layers is negligibly weak, so that every cross section of the 3D BZ at constant $k_z$ is essentially a copy of the 2D BZ of the film. In particular, the mirror invariant planes at $k_z = 0$ and $k_z = \pi$ [See Fig. 1(b)] should adopt the same MCN as the 2D TCI, and thus be indexed by $(\mu_1, \mu_2) = (n, n)$. For mirror symmetries inequivalent to $M_z$ (if any), the corresponding MCNs are all trivial $(0,0)$ because the mirror planes allowed by the layered geometry are normal to the films, and the crystalline surfaces respecting the mirror symmetries are essentially the 2D TCIs without metallic (surface) states. This means that the proposed TCI are characterized by the coupled MCNs $(n, n)$ for $M_z$ and $(0, 0)$ for any mirror symmetry inequivalent to $M_z$. Turning on the inter-layer interaction in a way that respects the mirror symmetry, the MCNs should persist within a finite range of the interaction, until the system experiences a topological phase transition through a gap closure [27], which can lead either to a new topological state where the indices are decoupled or to a conventional insulating state.

We demonstrate the topological phases associated with MCNs $(\mu_1, \mu_2)$ and their transitions from first principles by applying the above theory to a PbSe/h-BN heterostructure. Our calculation is performed with density functional theory (DFT) including the Perdew-Burke-Ernzerhof [28] generalized gradient approximation as implemented in the QUANTUM ESPRESSO package [29]. The atomic potentials are modeled by norm-conserving, optimized, designed nonlocal pseudopotentials with fully relativistic spin-orbit interaction generated by the OPIUM package [30, 31]. The wave functions are expanded in a plane-wave basis with an energy cutoff of 540 eV when calculating the surface band structure of PbSe(001) monolayers. The van der Waals interaction is described based on the semiempirical dispersion-correction DFT (DFT-D) method [32]. The tight-binding model, introduced in Ref. [10], is also employed to analyze the DFT results on (001) PbSe layers using parameter sets obtained from our DFT calculations. The results are consistent with the previous studies of IV-VI semiconductors, including PbSe [10, 23, 25]. The unit cell of the PbSe/h-BN heterostructure is generated by contracting the in-plane lattice constants of the h-BN sheet so that they match the pristine lattice constant of the PbSe. We have checked that the artificial contraction has negligible influence on the electronic structure near the Fermi energy, as h-BN has a wide band gap.

We first build a layered TCI based on (001) PbSe monolayers. Whereas PbSe is a trivial insulator in a 3D rocksalt geometry, (001) PbSe monolayer is expected to be a 2D TCI, indexed by the MCN $|\mu_{2D}| = 2$ [25]. As shown in Fig. 2(a), we consider a system consisting of PbSe monolayers stacked along the perpendicular direction to the plane ([001]-direction), so that Pb (and Se) atoms form chains along [001], separated by 8.9 Å. The other crystal parameters are set to those of the bulk PbSe. In this way, the inter-layer interaction remains weak, and the resulting system is a layered TCI indexed by (2, 2) associated with the (001) mirror plane. The system respects additional mirror symmetries about \{100\} and \{110\} mirror planes, on which the MCNs are all trivial as discussed above.

The calculated MCNs (2, 2) signal the presence of four surface states on the mirror-symmetric facets. As depicted in Fig. 2(b), for a surface containing $k_z$, the surface BZ has two inequivalent mirror-symmetric lines, $\Gamma - \Gamma - \overline{\Gamma} - \overline{\Gamma}$ and $\overline{\Gamma} - \overline{\Gamma} - \overline{\Gamma} - \overline{\Gamma}$ which are the projections of the 0 and $\pi$ mirror-planes into the surface plane. The absolute values of the MCNs $|\mu_1|$ and $|\mu_2|$ dictate the numbers of pairs of counter-propagating surface states on the $k_z = 0$ and $k_z = \pi$ mirror lines, respectively. It follows that there must exist two pairs of surface states along each line. To look for the surface states guaranteed by the
A h-BN sheet is a normal insulator which serves as spacer between the neighboring PbSe layers, as shown in Fig. 3(a). A h-BN sheet is a normal insulator with a wide band gap of 5 eV, which suggests that the band topology of the heterostructure should be governed by bands from the PbSe films. We find that the heterostructure has an equilibrium distance \( h_0 \) of 3.4 Å, with a binding energy of 0.08 eV per unit cell of PbSe, which indicates that the interaction is in the typical van der Waals regime.

In Fig. 3, we show the band structures of the PbSe/h-BN heterostructure along the high-symmetric lines in the BZ calculated for various PbSe-h-BN inter-layer distances \( h \). First, at equilibrium \( h_0 \), the system is found to be semi-metallic with a small hole pocket at \( X \) and \( Z \) plane. Then, by increasing the inter-layer distance from \( h_0 \) \( (h > h_0) \), the band gap at \( X \) keeps increasing, and the system eventually becomes an insulator when \( h > 3.5 \) Å. Increasing \( h \) further, we find that the system remains insulating without closing the band gap. Thus, we assign the layered TCI phase indexed by (2,2) to the system when \( h > 3.5 \).

Conversely, by decreasing the inter-layer distance from equilibrium \( h < h_0 \), which enhances the inter-layer interaction, we find that the system undergoes topological phase transitions signaled by the appearance of the Dirac points. As presented in Fig. 3(c), the Dirac points appear at \( h = 3.25 \) Å and \( h = 2.95 \) Å on the \( k_z = 0 \) plane and \( k_z = \pi \) mirror planes, respectively. The MCNs, calculated using all the valence bands on each mirror-symmetric plane, change from (2,2) to (0,2) and from (0,2) to (0,0) as \( h \) passes through 3.24 Å and 2.85 Å, respectively. All the topological phase transitions occur in a region where the system is a semimetal because of...
overlapping bands. Below $h = 2.77$ Å, the valence band maximum becomes higher in energy than the conduction band minimum on the $k_z = 0$ plane, so the MCN is not defined. Therefore, from the strong to weak inter-layer interaction regimes, four distinct topological phases appear, as shown in the phase diagram in Fig. 4(a): a trivial semimetal phase with $(0,0)$, a topological semimetal phase with $(\mu_1, \mu_2) = (0,2)$, a topological semimetal phase with $(\mu_1, \mu_2) = (2,2)$, and the layered TCI phase with $(\mu_1, \mu_2) = (2,2)$. Although the heterostructure of PbSe/h-BN sheets is expected to be semi-metallic at ambient pressure, we expect that these phases should be accessible under mechanical strain including the proposed (2,2) layered TCI or by inserting another h-BN sheet between PbSe layers. We also expect that the phase transitions demonstrated in this system should be representative of layered TCIs, and heterostructures of 2D TCIs can be considered as hosts of diverse topological phases accessible by engineering the inter-layer interaction. The calculated inter-layer distances may vary depending on details of the crystal geometry like a stacking registry between PbSe-h-BN layers, yet the qualitative features should remain intact.

Finally, we note that layered TCIs are analogous to weak topological insulators (TIs) \[33, 34\]. Weak TIs, characterized by zero $Z_2$ invariant yet non-zero weak topological indices $(\nu_1, \nu_2, \nu_3)$, is essentially a stack of 2D TI layers along the perpendicular direction that corresponds to $G = \nu_1 b_1 + \nu_2 b_2 + \nu_3 b_3$ in the BZ \[33\], having even numbers of robust Dirac cones at the surfaces perpendicular to the 2D TI layers \[34, 35\]. Similarly, 3D TCI with the same first and second mirror Chern numbers is like layered 2D TCIs, having $|\nu_1| + |\nu_2|$ Dirac cones on the surfaces normal to the 2D TCI layers. Also, like weak topological indices, $(\nu_1, \nu_2)$ are sensitive to the translational symmetry of the crystal. For instance, we find that a period-doubling along the $z$-axis changes the MCNs $(\mu_1, \mu_2)$: $(n,n) \rightarrow (2n,0)$, and $(n, -n) \rightarrow (0, 2n)$ due to the BZ folding, which can be induced by inter-layer bonding or a registry shift between 2D TCI layers. Indeed, we have found the MCNs to be $(4,0)$ when stacking the PbSe layers with a registry shift atoms between PbSe layers. We also expect that the phase transitions demonstrated in this system should be representative of layered TCIs, and heterostructures of 2D TCIs can be considered as hosts of diverse topological phases accessible by engineering the inter-layer interaction. The calculated inter-layer distances may vary depending on details of the crystal geometry like a stacking registry between PbSe-h-BN layers, yet the qualitative features should remain intact.

In conclusion, we propose new topological states of matter generated by stacking 2D TCIs, where simultaneous consideration of multiple MCNs is necessary. In the non-interacting limit between layers, the layered TCI phase emerges where the first and second MCNs $(\mu_1, \mu_2)$ are coupled. The layered TCI is a generic class of 3D TCIs which can apply to a range of 2D TCI materials. For example, a SnTe thin film, which is expected to be a 2D TCI when cleaved into an odd number of (001) layers $\geq 5$ \[23\], can play the role of the PbSe layer in the PbSe/h-BN heterostructure, thus realizing the layered TCI indexed by (2,2) when the layers are well separated. Apart from the non-interacting regime, we find topological semimetal phases indexed by (2,2) and (0,2) and trivial semimetal phase with (0,0). Despite the presence of metallic bulk states, the phase transitions should be observable via experimental techniques such as angle-resolved photoemission spectroscopy. Our findings shed light on the possibility of new TCI phases relying on the fact that a crystal in three dimensions can have multiple MCNs hosted on inequivalent mirror planes in reciprocal lattice. These may open the way towards the search for new topological materials, based on which quantum devices for electronics as well as spintronics can be built.

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\[1\] L. Fu, Phys. Rev. Lett. 106, 106802 (2011)
\[2\] M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010)
\[3\] X.-L. Qi and S.-C. Zhang, Rev. Mod. Phys. 83, 1057 (2011)
\[4\] C. Fang, M. J. Gilbert, and B. A. Bernevig, Phys. Rev. B 86, 115112 (2012)
\[5\] R.-J. Slager, A. Mesaros, V. Juricic, and J. Zaanen, Nature Physics 9, 98 (2013)
\[6\] C.-K. Chiu, H. Yao, and S. Ryu, Phys. Rev. B 88, 075142 (2013)
\[7\] C. Fang, M. J. Gilbert, and B. A. Bernevig, Phys. Rev. B 87, 035119 (2013)
\[8\] A. Alexandradinata, C. Fang, M. J. Gilbert, and B. A. Bernevig, Phys. Rev. Lett. 113, 116403 (2014)
\[9\] K. Shiozaki and M. Sato, Phys. Rev. B 90, 165114 (2014)
\[10\] T. H. Hsieh, H. Lin, J. Liu, W. Duan, A. Bansil, and L. Fu, Nat. Commun. 3, 982 (2012).
\[11\] P. Dziawa, B. J. Kowalski, K. Dybko, R. Buczko, A. Szczerbakow, M. Szot, E. Lusakowska, T. Balasubramanian, B. M. Wojek, M. H. Berntsen, O. Tjernberg, and T. Story, Nature Materials 11, 1023 (2012)
\[12\] T. Liang, Q. Gibson, J. Xiong, M. Hirschberger, S. P. Koduvayur, R. J. Cava, and N. P. Ong, Nat. Commun. 4, 2696 (2013).
\[13\] Y. Tanaka, T. Shoman, K. Nakayama, S. Souma, T. Sato, T. Takahashi, M. Novak, K. Segawa, and Y. Ando, Phys. Rev. B 88, 235126 (2013)
\[14\] Y. Okada, M. Serbyn, H. Lin, D. Walkup, W. Zhou, C. Dhital, M. Neupane, S. Xu, Y. J. Wang, R. Sankar,
F. Chou, A. Bansil, M. Z. Hasan, S. D. Wilson, L. Fu, and V. Madhavan, Science 341, 1496 (2013).

[15] S.-Y. Xu, C. Liu, N. Alidoust, M. Neupane, D. Qian, I. Belopolski, J. D. Denlinger, Y. J. Wang, H. Lin, L. A. Wray, G. Landolt, B. Slomski, J. H. Dil, A. Marckinkova, E. Morosan, Q. Gibson, R. Sankar, F. C. Chou, R. J. Cava, A. Bansil, and M. Z. Hasan, Nat. Commun. 3, 1192 (2012).

[16] Y. Sun, Z. Zhong, T. Shirakawa, C. Franchini, D. Li, Y. Li, S. Yunoki, and X.-Q. Chen, Phys. Rev. B 88, 235122 (2013).

[17] P. Tang, B. Yan, W. Cao, S.-C. Wu, C. Felser, and W. Duan, Phys. Rev. B 89, 041409 (2014).

[18] M. Kargarian and G. A. Fiete, Phys. Rev. Lett. 110, 156403 (2013).

[19] M. Kindermann, (2013), arXiv:1309.1667.

[20] H. Weng, J. Zhao, Z. Wang, Z. Fang, and X. Dai, Phys. Rev. Lett. 112, 016403 (2014).

[21] M. Ye, J. W. Allen, and K. Sun, (2013), arXiv:1307.1191.

[22] T. H. Hsieh, J. Liu, and L. Fu, Phys. Rev. B 90, 081112 (2014).

[23] J. Liu, T. H. Hsieh, P. Wei, W. Duan, J. Moodera, and L. Fu, Nature Materials 13, 178 (2014).

[24] H. Ozawa, A. Yamakage, M. Sato, and Y. Tanaka, Phys. Rev. B 90, 045309 (2014).

[25] E. O. Wrasse and T. M. Schmidt, Nano Lett. 14, 5717 (2014).

[26] J. C. Y. Teo, L. Fu, and C. L. Kane, Phys. Rev. B 78, 045426 (2008).

[27] J. C. Smith, S. Banerjee, V. Pardo, and W. E. Pickett, Phys. Rev. Lett. 106, 056401 (2011).

[28] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[29] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter. 21, 395502 (2009).

[30] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B 41, 1227 (1990).

[31] N. J. Rainer and A. M. Rappe, Phys. Rev. B 59, 12471 (1999).

[32] S. Grimme, J. Comput. Chem. 27, 1787 (2006).

[33] L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007).

[34] R. S. K. Mong, J. H. Bardarson, and J. E. Moore, Phys. Rev. Lett. 108, 076804 (2012).

[35] Z. Ringel, Y. E. Kraus, and A. Stern, Phys. Rev. B 86, 045102 (2012).