Design of Chern Insulating Phases in Honeycomb Lattices

Warren E. Pickett[1],* Kwan-Woo Lee[2,3],† and Rossitza Pentcheva[4‡]
[1]*Department of Physics, University of California, Davis, CA 95616, USA* [2]*Department of Applied Physics, Graduate School, Korea University, Sejong 33019, Korea*
[3] *Department of Display and Semiconductor Physics, Korea University, Sejong 33019, Korea*
[4]*Department of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 47057 Duisburg, Germany,*

(Dated: July 15, 2017)

The search for robust examples of the magnetic version of topological insulators, referred to as quantum anomalous Hall insulators or simply Chern insulators, so far lacks success. Our groups have explored two distinct possibilities based on multiorbital 3*d* oxide honeycomb lattices. Each has a Chern insulating phase near the ground state, but materials parameters were not appropriate to produce a viable Chern insulator. Further exploration of one of these classes, by substituting open shell 3*d* with 4*d* and 5*d* counterparts, has led to realistic prediction of Chern insulating ground states. Here we recount the design process, discussing the many energy scales that are active in participating (or resisting) the desired Chern insulator phase.

PACS numbers:

I. INTRODUCTION

In recent years the search for new materials with properties or electronic phases of interest has experienced a change of paradigm. The conventional method, referred to in the U.S. as the Edisonian method, is by (informed) trial and error. In fact Thomas Edison went as far as possible beyond the simplistic "trial and error" approach that is often brought to mind. He searched carefully in the databases that existed, he gave close attention to learning from earlier (successful, but also those dubbed failed) experiments, and he worked unceasingly toward specific goals – in his case, marketable properties and products. His approach was far from trial and error.

The recent paradigm change in the U.S. is promoted by the Materials Genome Initiative, a government-wide program to introduce computational expertise intimately into the materials development effort. The essence is to integrate computational capabilities into an integrated loop: computational design, synthesis of predicted materials, and characterization of properties to test whether desired aspects are present, with each point of the loop feeding back and forth with the computational node. Emphasis on computation is based on (i) the persistent and increasingly impressive progression of computer power, (ii) the demonstration that materials theory and its computational implementation leads to reliable predictions, and (iii) that this information (materials data) can be produced at a fraction of the cost and effort of laboratory exploration. Related efforts at computational design are active in other countries, judging from published papers.

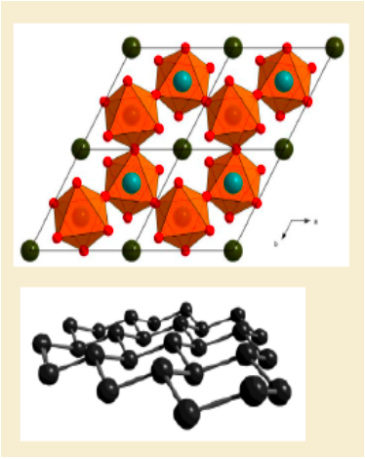

FIG. 1: (Color online) (top) View from above of the bilayer of (111) $LaXO_3$, illustrating the corner-sharing XO_6 octahedra. Alternate octahedra are centered at different heights. (bottom) Perspective view of the buckled honeycomb X bilayer sublattice.

One outgrowth of this new paradigm is the "high throughput" approach:[1] choose a viable computational algorithm, identify a *descriptor* (or a few), that is, a computable property that is essential to the desired application, then to search classes of materials thought to be likely candidates – this may be thousands of materials – and sort through results to find promising candidates.

*Electronic address: pickett@physics.ucdavis.edu
†Electronic address: mckwan@korea.ac.kr
‡Electronic address: rossitza.pentcheva@uni-due.de

This approach can be successful when the number of degrees of freedom in the materials is understood and limited, when the descriptor is clear, and the algorithm can be automated. Access to considerable computer time can often be obtained, and the procedure can be implemented and optimized.

Some important problems cannot be approached so directly. Suppose one wishes to find, or design, a new high temperature superconductor, following the leads of the cuprates and Fe-pnictides and -chalcogenides which neighbor magnetic phases. This is really challenging, since there is no theory in these two classes of superconductors that specifies just what descriptor(s) one should adopt. In these attempts, choices focus on similarities of crystal structure or electronic structure, or on similar magnetic phases neighboring the superconductors. The few efforts in this area have not yet produced positive results, though they are still in the early stage.

In the last few decades, the two-dimensional (2D) honeycomb lattice has attracted interest due to several exotic physical phenomena related with superconductivity, novel magnetic states, and topological phases, some of them building on the Dirac point 2D material graphene. Recently, discoveries of topological insulators, originally on the honeycomb lattice,[2] have stimulated increased research on properties of systems with honeycomb lattices.[3–6]

The design and discovery of Chern insulators, the magnetic version of topological insulators (TIs), is one of the current forefront pursuits in research on topological materials. Unlike their time-reversal symmetric cousins, the non-magnetic Z_2 TIs characterized[2] by topological indices $\nu_0(\nu_1\nu_2\nu_3)$ which can be only zero or one, the Chern number $\mathcal{C}$ can be any integer. Aside from the obvious interest, and complication, of being a magnetic system, this unbounded aspect of values of $\mathcal{C}$ provides new topological behavior to explore and perhaps exploit. One clear feature is that, while the bulk is insulating, there are $\mathcal{C}$ boundary bands crossing the gap. These bands provide the quantum anomalous Hall effect, thus a larger $\mathcal{C}$ will provide a correspondingly larger Hall response.

The initial expectation of realizing a Chern insulator was to incorporate some magnetic ions onto or within a TI,[7] or layering transition metal oxides.[8–10] Several hurdles have impeded the first approach. First, most known TIs have very small gaps (a few meV), complicating the studies. Second, it is unfortunate that known TIs are not truly insulating in the bulk due to defects, hence the TI-specific boundary state behavior becomes challenging to separate from bulk contributions. Third, several proposals have suggested submonolayers of magnetic ions or nonstoichiometric additions of magnetic ions, whereby disorder and non-stoichiometry provide experimental challenges. Synthesis and characterization of such materials presents its own challenges.

These complications and limitations may be alleviated by turning to (1) stoichiometric systems, and (2) wider gap materials. For these reasons, transition metal oxides (TMOs) provide promise. Bandgaps can be expected to be larger, and a great deal of expertise in the synthesis of both bulk and layer-by-layer grown oxides has accumulated. (Even so, Chern insulators built on TMOs also may have only small gaps.[11–13]) Along with these positive aspects, TMOs provide a grand palette of possibilities, many of which offer interplay among lattice, spin, and orbital degrees of freedom, together with correlation effects and spin-orbit coupling (SOC), thus providing an enormous field to explore and exploit. Along with this large playing field comes a variety of challenges. Here we discuss succinctly our experience in the context of two honeycomb lattice systems.

II. TWO HONEYCOMB LATTICES

The two lattices we have studied display some differences. First, we should mention commonalities. The ideal honeycomb lattice has features that distinguish it from the common square lattice. It has two sites per cell (sublattices A and B), making it intrinsically multiorbital. The sublattice ("valley") degree of freedom has been exploited widely in the study of graphene. The local symmetry of each site is threefold, which incorporates its own aspects. One is that the t_{2g} subshell on a transition metal ion is represented conveniently by the linear combinations

$$\phi_m = \frac{1}{\sqrt{3}}(\xi_m^0 d_{xy} + \xi_m^1 d_{yz} + \xi_m^2 d_{zx}), \qquad (1)$$

where the phase factor is $\xi_m = exp(i\frac{2\pi m}{3})$, $m =< L_z >$ is the projection of the orbital moment, and the superscript is an exponent. There is the fully symmetric (with respect to threefold rotations) member a_{1g} (m=0) and a pair of complex e_g' orbitals ($m = \pm 1$). This distinction from real xy, yz, zx orbitals becomes crucial[3] when SOC is active, and more especially so for the magnetic ions we are pursuing.

Both systems we have studied have open shell transition metal ions on the 2D honeycomb lattice sites, so each sublattice itself is multiorbital. Experience in related TMOs has been important.[14–16] We note that the density functional theory for correlated materials DFT+U method is necessary to model the gap in transition metal oxides, here U is the intra-atomic Coulomb repulsion (Hubbard) energy. We have used all-electron, full potential methods in our studies.[17, 18] $BaFe_2(PO_4)_2$ has the ideal honeycomb Fe sublattice[19–21] for which sublattice symmetry breaking is not an important factor.[22, 23] The other is comprised of a (111) bilayer of X cations encased in the perovskite insulator $LaAlO_3$ (denoted 2LXO/LAO), forming a buckled honeycomb lattice,[24, 25] illustrated in Fig. 1. The transition metal X ion sits, in the idealized structure, at a site of local cubic symmetry within an O_6 octahedron, but further neighbors (or structural relaxation) reduces symmetry to trigonal and even lower, as broken symmetries proliferate.

Transition metal ions are prone to develop magnetic moments, after which SOC will induce an orbital magnetic moment.[26, 27] Breaking of spin, orbital, sublattice, etc. symmetry is accompanied by geometric distortion and perhaps caused by it, enlarging the set of degrees of freedom. These degrees include charge order, spin imbalance, orbital polarization and orbital ordering, structural distortion, and perhaps more exotic quantum order parameters although we have not pursued that possibility.

The energy scales are several, providing rich behavior but challenges for material design. The bandwidth W of the active orbitals; on-site Coulomb repulsion U; Hund's magnetic coupling J; crystal field splitting Δ_{cf}; trigonal crystal subfield splitting δ_{cf}; SOC coupling strength ξ; Jahn-Teller distortion energy(s). Evidently the complications are many. In such a broad field of possibilities, it is beyond current understanding to define a descriptor, or a few of them, that will allow a computer code to evaluate whether a given case is near a Chern insulator, or not. This is a problem that invites intimate human-machine interaction.

A. Chern-ness in the Ising Ferromagnet BFPO

To summarize briefly: in $BaFe_2(PO_4)_2$ it was necessary to include U together with SOC to realize any appreciable gap. A transition from Chern insulator at small U to trivial Mott insulator at larger U occurred at a bandgap closing and reopening for the critical value U_c=2.45 eV. Since calculated values of U for Fe are 4-5 eV, our conclusion was that the ground state is a conventional Mott insulator. It is noteworthy that the topological transition coincides[22, 23] with a transition from a small orbital moment on Fe to a value of 0.7-0.8 μ_B, an extremely large value for a 3d ion and near the 1 μ_B limit for the t_{2g} subshell. It is natural to suspect a connection, if not a causal relationship. This large moment is accompanied by a very large calculated magnetocrystalline anisotropy energy, which also accounts for the observed Ising nature of the ferromagnetic state.

B. Chern-ness in the 2LXO/LAO system

Our initial focus on 3d ions led us to obtain the ground states for the entire 3d series 2LXO/LAO, X=Ti, V, Cr, Mn, Fe, Co, Ni, Cu. All are magnetic, and those with filled subshells are structurally stable and uninteresting. An open subshell led, depending on band filling, to charge ordering, orbital ordering, and in some cases structural distortion, all typical Mott behavior. Before accounting for SOC, the Ti, Mn, and Co cases displayed Dirac points in their majority band structure. SOC broke symmetry and resulted in gap opening, closely associated with the breaking of sublattice symmetry by the various order parameters. These systems relaxed through a Chern insulating phase, but the distortions were too large; before becoming fully relaxed, the gap closed and band inversion disappeared, and the ground states were conventional, albeit symmetry broken Mott insulators.

The reasoning – the resulting design principles – will be discussed a little more in the next section. An evident conclusion was that the distortion, though unavoidable in this system, is not destructive but is too severe. This tendency could be combatted by decreasing the tendency toward Jahn-Teller distortion, which is related to localization of the orbitals, and by increasing SOC strength which would serve to retain band entanglement to larger gap values. Calculations extended to the 4d and 5d cations that followed led to the prediction[27] of Chern insulating ground states in the 4d X=Ru compound (Chern number $\mathcal{C}$=-1, a gap of 130 meV) and the 5d Chern insulator X=Os ($\mathcal{C}$=2, gap of 50 meV). It is noteworthy that each of these has a modest value of orbital moment of 0.16-0.19 μ_B, especially since magnetic 5d ions have shown many times to display larger orbital moments.

III. DISCUSSION AND SUMMARY

Chern insulators arise from (ferro)magnetic materials in which spin-orbit interactions open a gap, leaving "inverted bands." This last item is not transparent in the electronic structure; one simply must calculate the Berry curvature and integrate it over the zone, and if it is nonzero (it will be an integer) then the bands are inverted. The character of the bands that is essential in providing a fruitful Berry connection needs further study. When it is a sum over occupied bands (which is common) the critical characteristic – a topological one – is even more elusive.

Our analysis of the evolution of the electronic system, versus interaction strength U for $BaFe_2(PO_4)_2$, and versus structural distortion (related to U) provided the necessary guidance for successful design of Chern phases in buckled honeycomb lattices, but unfortunately without making the microscopic mechanism evident. The emerging design principles became for us

- study honeycomb lattices. This is not a criterion, but they provide an intrinsic richness not shared by simpler, single site lattices.
- focus on systems that promote a Dirac point at K in the symmetric phase; recall that a Dirac point provides a singularity in the topological nature of the system,
- avoid large symmetry-breaking effects such as the Jahn-Teller distortions that open large gaps and destroyed the Chern phases in the 3d systems,
- vary the strain to obtain optimal values, because electronic configurations are sensitive to strain,
- increase the SOC strength, as it sustains the band entanglement over a proportionately greater energy and can be expected to retain entanglement with larger gap.

The Dirac point aspect seems to be one unifying underlying feature in the systems we have studied. The interac-

tion strength U, which also tends to enforce anisotropic, Jahn-Teller-active ions, appears to be a strong player. Sensitivity to strain: this item reflects the many studies which reveal that strain can strongly influence electronic systems, by providing symmetry-breaking forces that spur, for example, orbital polarization with its important consequences. An increase in SOC strength has been widely postulated as a positive influence, making $5d$ systems one focus of searches for Chern insulators. These concepts are guiding our further studies on this topic.

Acknowledgments.‘ This research was supported by National Research Foundation of Korea Grant No. NRF-2016R1A2B4009579 (K.W.L), by U.S. NSF DMREF Grant DMR-1534719 (W.E.P.), and by the German Science Foundation within SFB/TR80, project G3 (R.P.).

[1] D. Morgan, G. Ceder, S. Curtarolo, High-throughput and data mining with ab initio methods, Measurement Sci. and Tech. **16**, 296 (2005).
[2] C. L. Kane and E. J. Mele, Z_2 Topological Order and the Quantum Spin Hall Effect. Phys. Rev. Lett. **95**, 146802 (2005).
[3] A. Rüegg and G. A. Fiete, Topological insulators from complex orbital order in transition-metal oxides heterostructures. Phys. Rev. B **84**, 201103(R) (2011).
[4] A. Shitade, H. Katsura, J. Kuneš, X.-L. Qi, S.-C. Zhang, and N. Nagaosa, Quantum Spin Hall Effect in a Transition Metal Oxide Na_2IrO_3. Phys. Rev. Lett. **102**, 256403 (2009).
[5] M. Zhou, Z. Liu, W. Ming, Z. Wang, and F. Liu, sd^2 Graphene: Kagome Band in a Hexagonal Lattice, Phys. Rev. Lett. **113**, 236802 (2014).
[6] R. Nandkishore, L. S. Levitov, and A. V. Chubukov, Chiral superconductivity from repulsive interactions in doped graphene, Nature Phys. **8**, 158 (2012).
[7] C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Phys. Rev. Lett. **101**, 146802 (2008).
[8] K. F. Garrity and D. Vanderbilt, Chern insulators from heavy atoms on magnetic substrates, Phys. Rev. Lett. **110**, 116802 (2013).
[9] S. Baidya, U. V. Waghmere, A. Paramekanti, and T. Saha-Dasgupta, High-temperature large-gap quantum anomalous Hall insulating state in ultrathin double perovskite films, Phys. Rev. B **94**, 155405 (2016).
[10] H. P. Wang, W. Luo, and H. J. Xiang, Prediction of high-temperature quantum anomalous Hall effect in two-dimensional transition metal oxides, Phys. Rev. B **95**, 125430 (2017).
[11] V. Pardo and W. E. Pickett, Half-metallic semi-Dirac Point Generated by Quantum Confinement in TiO_2/VO_2 Nanostructures, Phys. Rev. Lett. **102**, 166803 (2009).
[12] H. Huang, Z. Liu, H. Zhang, W. Duan, and D. Vanderbilt,, Emergence of a Chern-insulating state from a semi-Dirac dispersion, Phys. Rev. B **92**, 161115(R) (2015.)
[13] Cai, T., X. Li, F. Wang, S. Ju, J. Feng, and C.-D. Gong, Single-spin Dirac Fermion and Chern insulator based on simple oxides, *Nano Lett.* **15**, 6434 (2015).
[14] H.-S. Jin, K.-H. Ahn, M.-C. Jung, and K.-W. Lee, Strain and spin-orbit coupling induced orbital ordering in the Mott insulator $BaCrO_3$, Phys. Rev. B **90**, 205124 (2014).
[15] D. Doennig, W. E. Pickett, and R. Pentcheva, Massive Symmetry Breaking in $LaAlO_3/SrTiO_3(111)$ Quantum Wells: A Three-Orbital, Strongly Correlated Generalization of Graphene, Phys. Rev. Lett. **111**, 126804 (2013).
[16] D. Doennig, W. E. Pickett, and R. Pentcheva, Confinement-driven transitions between topological and Mott phases in $(LaNiO_3)_N/(LaAlO_3)_M(111)$ superlattices, Phys. Rev. B **89**, 121110(R) (2014).
[17] K. Koepernik and H. Eschrig, Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme, Phys. Rev. B **59**, 1743 (1999).
[18] K. Schwarz and P. Blaha, Solid state calculations using WIEN2k, Comput. Mater. Sci. **28**, 259 (2003).
[19] H. Kabbour, R. David, A. Pautrat, H.-J. Koo, M.-H. Whangbo, G. André, and O. Mentré, A genuine two-dimensional Ising ferromagnet with magnetically driven re-entrant transition, Angew. Chem. Int. Ed. **51**, 11745 (2012).
[20] R. David, A. Pautrat, D. Filimonov, H. Kabbour, H. Vezin, M.-H. Whangbo, and O. Mentré, Across the structural re-entrant transition in $BaFe_2(PO_4)_2$: influence of the two-dimensional ferromagnetism, J. Am. Chem. Soc. **135**, 13023 (2013).
[21] R. David, H. Kabbour, D. Filimonov, M. Huvé, A. Pautrat, and O. Mentré, Reversible topochemical exsolution of iron in $BaFe_2^{2+}(PO_4)_2$, Angew. Chem. Int. Ed. **53**, 13365 (2014).
[22] Y.-J. Song, K.-W. Lee, and W. E. Pickett, Large orbital moment and spin-orbit enabled Mott transition in the Ising Fe honeycomb lattice of $BaFe_2(PO_4)_2$, Phys. Rev. B **92**, 125109 (2015).
[23] Y.-J. Song, K.-H. Ahn, W. E. Pickett, and K.-W. Lee, Tuning ferromagnetic $BaFe_2(PO_4)_2$ through a high Chern topological phase, Phys. Rev. B **94**, 125134 (2016).
[24] D. Xiao, W. Zhu, Y. Ran, N. Nagaosa, and S. Okamoto, Interface engineering of quantum Hall effects in digital transition metal oxide heterostructures, Nat. Commun. **2**, 596 (2011).
[25] A. M. Cook and A. Paramekanti, Double Perovskite Heterostructures: Magnetism, Chern Bands, and Chern Insulators, Phys. Rev. Lett. **113**, 077203 (2014).
[26] D. Doennig, S. Baidya, W. E. Pickett, and R. Pentcheva, Design of Chern and Mott insulators in buckled 3d-oxide honeycomb bilayers, Phys. Rev. B **93**, 165145 (2016).
[27] H. Guo, S. Gangopadhyay, O. Koeksal, R. Pentcheva, and W. E. Pickett, Wide gap Chern Mott insulating phases achieved by design, npj Quantum Materials **2**, 4 (2017).