Comment on "Topological Insulators in Ternary Compounds with a Honeycomb Lattice"

The Letter by Zhang *et al.* [1] predicted, on a purely theoretical bases, the existence of a family of topological insulators (TIs). This family can be seen as a relative of graphite and crystallizes in a honeycomb lattice (space group $P6_3/mmc$, no. 194). Keeping this structure, the authors tried many ternary combinations by replacing the three chemical elements. However, the honeycomb structure of Ref. [1] is dynamically unstable for some of the proposed materials, including the key example LiAuSe, whose true ground state does not display TI properties.

To explore the potential energy surface of these compounds we used the minima hopping method [2], an efficient crystal structure prediction algorithm designed to obtain the low-energy phases of a system given solely its chemical composition. We used cells containing 1, 2, and 3 formula units (up to 9 atoms), and forces and energies were obtained using density functional theory as implemented in the code VASP [3] with the Perdew-Burke-Ernzerhof approximation [4] to the exchange-correlation functional. Because of the large computational burden required by this procedure, we concentrated our efforts on two compounds, namely, LiAgSe and LiAuSe. According to Ref. [1] these two are predicted to be TIs.

In Fig. 1 we show the energy per formula unit of LiAgSe as a function of the volume for the most stable structures found in our simulations, in comparison with the reference $P6_3/mmc$ honeycomb lattice of Ref. [1]. The ground state is a cubic crystal with 3 atoms in the unit cell (space group $F\bar{4}3m$, no. 216). The $P6_3/mmc$ structure of Ref. [1] is considerably higher in energy, and many structures (not all shown) lie between it and the ground state. Furthermore, the C44 elastic constant of the $P6_3/mmc$ crystal is negative (-5.3 GPa), which shows that it is dynamically unstable, while the three lowest structures we found ($F\bar{4}3m$, $P4/nmm$, and $P4_2/mmc$) follow the Born elastic conditions of stability. Finally, minima hopping simulations at finite pressure reveal that the $P6_3/mmc$ structure is not stabilized by low pressure.

The band gap of the ground-state structure $F\bar{4}3m$ is 0.28 eV within Kohn-Sham density functional theory, an order of magnitude larger than the one of the reference structure which was 1 meV. Analyzing the band inversion at different time-reversal symmetry, we conclude that this compound is not a TI. Since the band gap is already large enough, we do not need more accurate calculations, such as GW [5].

We obtained strictly analogous results for LiAuSe. Again, the lowest energy structure does not correspond to the one published in Ref. [1]. The ground state, a layered structure with 6 atoms in the unit cell (space group $P2/c$, no. 13), has a band gap of 0.4 eV and is not a TI.

Even if Ref. [1] is an important step forward in the design of new TIs, we conclude that LiAgSe and LiAuSe, predicted to be TIs, are not TIs. This result calls
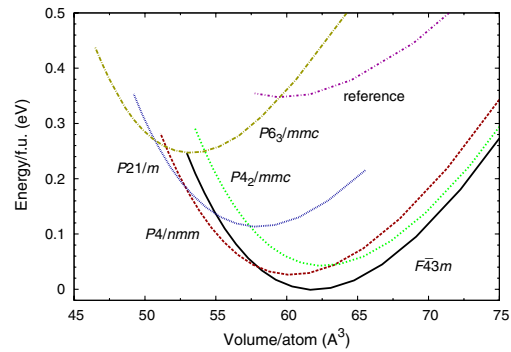

FIG. 1 (color online). Total energy per formula unit as a function of the volume for several crystal structures of LiAgSe. Note that the $P6_3/mmc$ line is not the reference structure of Ref. [1].

for a further systematic check of the other reported hypothetical TIs. This example teaches the general lesson that the simple substitution of "similar" chemical elements should always be performed with care, as it does not necessarily lead to ground-state structures, and it can even lead to dynamically unstable structures. In conclusion, reliable structural prediction tools for the ground state and rigorous stability analysis (elastic constants and phonons) are *sine qua nons* whenever novel stuctures are theoretically proposed.

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