Topologically nontrivial phases in superconducting transition metal carbides

Richard Zhan and Xuan Luo
National Graphene Research and Development Center, Springfield, Virginia 22151, USA

(Dated: October 30, 2018)

Topological superconductors have shown great potential in the search for unique quasiparticles such as Majorana fermions. Combining nontrivial band topology and superconductivity can lead to topological superconductivity due to the proximity effect. In this work, we used first principle calculations to predict that rocksalt phases of VC and CrC are superconducting with topologically nontrivial states. The phonon dispersions of these transition metal carbides displayed no imaginary frequencies, which suggests dynamic stability. Therefore, these transition metal carbides are practical candidates for studying topological superconductors and their associated Majorana bound states.

I. INTRODUCTION

Quantum computing has gained interest in recent years due to its potential to disrupt many different fields including biology [1], chemistry [2], and computer science [3]. One of the biggest challenges of creating a practical quantum computer is the effect of environmental noise on its calculations. Topological quantum computers are a possible solution to this issue. These devices use Majorana fermions (MFs) to encode information that is invariant to local perturbations [4]. However, realizing MFs has proven difficult since the initial prediction of their existence in 1937 by Ettore Majorana. On the other hand, MFs have been predicted to bind to defects in certain superconductors (SC), creating Majorana bound states (MBS) [5].

One way to observe these MBSs is with topological superconductors (TSC). MBS exist in the normal core of quantum vortices as well as on the boundaries of magnetic domains in TSCs. Therefore, studying MBSs in TSCs may help advance the creation of practical quantum computers [6]. Previous studies have identified multiple ways to achieve topological superconductivity. One approach to topological superconductivity uses proximity effect induced superconductors. When a topological insulator or semiconductor with Rashba spin-orbit coupling (SOC) is brought into contact with an s-wave SC, the interface turns into a TSC [7, 8]. Previous studies have produced promising results for these topologically superconducting heterostructures (TSH). In 2014, the first TSH was experimentally realized [9]. One year later, researchers observed MBSs in the same TSH of Bi2Te3/NbSe2 [10]. TSHs, however, can be complex and consequently difficult to create, which hinders further research into these types of TSCs. In addition, most TSHs have relatively low SC transition temperatures, usually below 4 K [11].

Recent work has successfully brought together the two fundamental aspects of TSCs in a single material, the topological nature of the band structure and superconductivity. Materials such as Au2Pb [12, 13], CsSn3 [14], Mg2Pb [15], and MoC [11] have been predicted to be superconducting and have topologically nontrivial band structures. α-MoC, a transition metal carbide, was one of the most promising materials due to its relatively high \( T_c \) of 14 K. One of the most promising rock-salt transition metal carbides is CrC with predicted critical temperatures ranging from 25-39 K [16, 17]. Additionally, advances in synthesizing rock-salt CrC [18] further increases the practicality of studying this compound.

In this study, we use first-principle calculations to determine the electronic band structure of the superconductors VC, CrC, NbC, and TaC. We show that VC and CrC are potential candidates for studying topologically superconductivity by calculating their \( Z_2 \) topological invariants. In addition, the phonon band structures were calculated to show the stability of these materials. So, these compounds are promising candidates for studying topological superconductors and their associated MBSs.

Our methods for our first principle calculations can be found in Section II. We present and discuss our results on the topological superconductivity of VC and CrC are located in Section III. Finally, our conclusion is found in Section IV.

II. METHOD

A. Computational Details

The density functional theory [19, 20] (DFT) calculations were performed with ABINIT [21, 22]. We used generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functionals [23] and projector augmented wave (PAW) pseudopotentials [24] in our calculations. The PAW pseudopotentials were generated using AtomPAW [25]. The electron configuration and cutoff radius for the pseudopotentials of each element used in our calculations are shown in Table I. We used the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization [29, 33] for structural optimization. The \( Z_2 \) topological invariants and Wilson loops were calculated with ABINIT and Z2Pack [34, 35]. The phonon frequencies were calculated using density functional perturbation theory (DFPT). We used local density approximation (LDA) plane wave exchange correlation functionals for the DFPT calculations.
TABLE I: Each element’s valence electron configuration and radius cutoff used in generating the PAW pseudopotentials.

| Element | Valence Configuration | Cutoff Radius (Bohr) |
|---------|----------------------|---------------------|
| C       | \(2s^22p^2\)         | 1.51                |
| V       | \(3s^24s^23p^63d^3\) | 2.20                |
| Cr      | \(3s^24s^13p^63d^5\) | 2.11                |
| Nb      | \(4s^25s^14p^64d^4\) | 2.21                |
| Ta      | \(5s^26s^25p^65d^3\) | 2.41                |

B. Total Energy Convergence

The plane-wave kinetic energy cutoff and k-point grid of each compound were converged after they reached the tolerance criteria of \(10^{-4}\) Ha twice successively. The energy cutoff and k-mesh we used for each compound can be found in Table II. In our DFPT calculations, we used \(16 \times 16 \times 16\) k-point grid and a \(8 \times 8 \times 8\) q-point grid. We used a broadening factor \((\sigma)\) of 0.005 Ha for the Gaussian smearing described by the following equation.

\[
\tilde{\delta}(x) = \frac{e^{-x^2}}{\sqrt{\pi} \sigma}, \quad x = \frac{\epsilon - \epsilon_F}{\sigma}
\]

TABLE II: Each compound’s converged kinetic energy cutoff and k-point grid for the GGA and LDA pseudopotentials

| Compound | Energy Cutoff (Ha) | K-Point Grid |
|----------|-------------------|--------------|
| VC       | 17\(^*\)          | \(6 \times 6 \times 6\) |
| CrC      | 23                | \(6 \times 6 \times 6\) |
| NbC      | 24                | \(14 \times 14 \times 14\) |
| TaC      | 24                | \(18 \times 18 \times 18\) |

\(^*\) All of the convergence tests resulted in the same values for both GGA and LDA pseudopotentials except for kinetic energy cutoff of VC. It was determined to be 17 Ha for GGA and 16 Ha for LDA.

C. Band Structure

We used the high-symmetry points \(\Gamma (0, 0, 0), X (0, 0.5, 0.5), L (0.5, 0.5, 0.5), W (0.25, 0.75, 0.5), U (0.25, 0.625, 0.625), \) and \(K (0.375, 0.75, 0.375)\) shown in Figure 1(b). Our k-point sampling \(16 \times 16 \times 16\) was generated with the shifts \((0.5, 0.5, 0.5), (0.5, 0, 0), (0, 0.5, 0),\) and \((0, 0, 0.5)\). We calculated band structures with and without SOC for each material.

III. RESULTS AND DISCUSSION

We investigated the properties of various transition metal carbides including VC, CrC, TaC, and NbC. First, we conducted total energy convergence tests on each of their energy cutoffs and k-point grids. Then, we performed relaxation on their lattice parameters. Afterwards, the band structures, densities of states (DOS), and partial densities of states (PDOS) with and without SOC were calculated. We compared our band structures without SOC to other studies, since previous research generally did not include relativistic effects in their calculations. The Wilson loops and \(Z_2\) topological invariants were calculated for each material as well. Finally, we calculated the phonon dispersions of each compound to determine their stability.

A. Lattice Parameters

We performed BFGS optimization on the lattice parameters of each materials primitive cell. Since the atoms in rock-salt structures are fixed due to high symmetry, we used a potential residual tolerance of \(10^{-12}\) Ha as our stopping criteria for the self-consistent field cycles during relaxation. Table III compares experimental determined lattice parameters with our theoretically calculated lattice parameters. Our GGA parameters were in very good agreement with experimental values. The lattice parameters calculated with LDA were underestimates as expected. The reduced atomic coordinates of the rock-salt structure are \((0, 0, 0)\) and \((0.5, 0.5, 0.5)\). Both atoms in the rock-salt structure can serve as inversion centers.

B. Electronic Band Structure

Figure 2(a) depicts the band structure of VC, not including the effects of SOC. It has two band crossings in
FIG. 2: The yellow highlighted region depicts the band gap (Color available online). (a) The band structure of VC without SOC. (b) The band structure and DOS of VC with SOC. (c) Magnified view of the red box in (a). (d) Magnified view of the red box in (b). (e) The band structure of CrC without SOC. (f) The band structure and DOS of CrC with SOC. (g) Magnified view of the red box in (e). (h) Magnified view of the red box in (f).

TABLE III: Experimental vs. our theoretically calculated lattice parameters for each material.

| Compound | Experimental (Å) | GGA (Å) | LDA (Å) |
|----------|------------------|---------|---------|
| VC       | 4.16294a         | 4.162   | 4.094   |
| CrC      | 4.03b            | 4.064   | 4.010   |
| NbC      | 4.45443c, 4.470c | 4.484   | 4.426   |
| TaC      | 4.45300a, 4.457d | 4.477   | 4.412   |

a Reference [37]  
b Reference [38]  
c Reference [39]  
d Reference [40]

The band structure of NbC without SOC is depicted in Figure 3(a). Our NbC band structure is consistent with the $Z_2$ topological invariant. Our DOS is also in very good agreement with earlier studies [41] [43]. The DOS diagram shows that VC is metallic, like most transition metal carbides. The regions near the Fermi level are almost completely dominated by the V-p orbitals, aside from a small contribution by the C-p orbitals between 2-2.5 eV.

CrC’s band structure without SOC is found in Figure 2(e) and is extremely similar to that VC’s band structure. It compares well with other studies [17, 44]. There are two band crossings between X and W (Figure 2(g)). When the effects of SOC are included, the overall band structure remains similar to before due to the weak SOC of the chromium and carbon atoms (Figure 2(f)). Even so, the two previous band crossings are gapped by SOC (Figure 2(h)). Consequently, CrC may have a nontrivial band topology. Doping CrC with 2 electrons per primitive cell would raise the Fermi level, so the topologically nontrivial bands could be accessed. CrC’s DOS reveals that it is also a metal, and its metallic properties arise from the transition metal atoms’ d-orbitals. When compared to VC, the additional d-orbital electron in Cr results in a downward shift of the DOS. This shift leads to a higher DOS at the Fermi level in CrC. Both our DOS and PDOS agree with earlier calculations [17, 41, 45].

The band structure of NbC without SOC is depicted in Figure 3(a). Our NbC band structure is consistent with
FIG. 3: The yellow highlighted region depicts the band gap. (a) The band structure of NbC without SOC. (b) The band structure and DOS of NbC with SOC. (c) Magnified view of the red box in (a). (d) Magnified view of the red box in (b). (e) The band structure of TaC without SOC. (f) The band structure and DOS of TaC with SOC. (g) Magnified view of the red box in (e). (h) Magnified view of the red box in (f).

previous studies [46, 47]. When SOC is not taken into account, NbC’s band structure has two band crossings: one at Γ − X and another at X − W (Figure 3(c)). Thus, the band structure of NbC without SOC does not have a band gap. Once again, the weak SOC of the niobium and carbon atoms changes little in the overall band structure (Figure 3(b)). However, a small band gap opens in the previous two band crossings at Γ − X and X − W, leading to a continuous region with direct gaps (Figure 3(d)). The SOC-induced band gaps strongly suggest that NbC possesses a topologically nontrivial band structure. Since there is a large amount of overlap between the valence and conduction bands, NbC is clearly a metal. Other studies’ DOS are comparable to ours [46, 48, 49].

Figure 3(e) shows that TaC’s band structure without SOC has many similarities to NbC. The 22nd and 23rd bands intersect twice in the same regions as before (Figure 3(g)). This is also consistent with earlier research [50, 51]. Including SOC in our band structure calculation causes the two crossings to become gapped (Figure 3(h)). A previous study also found the same effect in TaC [51]. Since Ta atoms have stronger spin-orbit coupling than Nb atoms, the SOC-induced gapping in TaC is much greater than the gapping in NbC (Figure 3(f)). The presence of SOC gapping implies that the band structure of TaC is topologically nontrivial. TaC has a region of suppressed DOS near 4 eV which also occurred in other studies [50, 51].

C. Topological Invariance

The Wilson loop method can also be used to calculate the \( \mathbb{Z}_2 \) topological invariant of both centrosymmetric and noncentrosymmetric structures. Figure 4 displays the Wilson loops of VC, CrC, NbC, and TaC at the plane \( k_z = 0 \) and \( k_z = \pi \). Using Z2Pack, we calculated that in VC and CrC an odd number of Wannier charge centers (WCCs) are crossed when traversing the path created by matching up each of the middles of the largest WCC gaps. So, the \( \mathbb{Z}_2 \) topological invariants of VC and CrC are 1, indicating that they contain topologically nontrivial bands. However, for NbC and TaC, their Wilson loops showed an even number of crossings, so they likely are not topologically nontrivial.

D. Phonon Band Structure

Figure 5(a) depicts the phonon band dispersion of VC. Our acoustic bands are triply degenerate at the L point while another study found doubly degenerate bands [52]. Since NbC’s phonon band structure has no imaginary component, VC in the rock-salt structure is stable. This
is consistent with experimental synthesis of stoichiometric VC. Advances in synthesizing VC further increases the usefulness of this material [53, 54]. Therefore, VC may be able to serve as a practical platform for studying topological superconductivity.

The phonon dispersion of CrC is shown in Figure 5(b). Our calculated phonon dispersion has the same features as previous studies aside from a small discrepancy at the X point [17]. Our quantitative values are also fairly accurate. We calculated the transverse optical frequency at Γ to be 14.702 THz, compared to 13.49 THz and 15.6 THz from other studies [17, 45]. We confirm a previous study which reported that CrC is dynamically stable [17]. Consequently, the dynamical stability, topological bands, and high $T_c$ of CrC makes it a strong candidate for future research in the field of topological superconductivity.

ACKNOWLEDGEMENTS

We thank Dr. Gefei Qian for providing technological support. We also greatly appreciate Prof. Shengbai Zhang for helpful discussions.

IV. CONCLUSION

In summary, we have used first-principle calculations to theoretically predict the presence of topologically nontrivial band structures in VC and CrC. The SOC-induced gapping in each of these material’s band structures suggests nontrivial band topology. Additionally, the Wilson loops for each material were calculated. Both VC and CrC had nonzero $Z_2$ topological invariants while NbC and TaC had $Z_2$ topological invariants of 0. We also calculated the phonon band structures of VC and CrC to confirm that each material was dynamically stable. Since their phonon dispersions displayed no imaginary frequencies, they are both stable compounds.
FIG. 5: (a) Phonon dispersion of VC. (b) Phonon dispersion of CrC.

[1] A. Perdomo-Ortiz, N. Dickson, M. Drew-Brook, G. Rose, and A. Aspuru-Guzik, Scientific Reports 2, 571 (2012).
[2] B. P. Lanyon, J. D. Whitfield, G. G. Gillett, M. E. Goggin, M. P. Almeida, I. Kassal, J. D. Biamonte, M. Mohseni, B. J. Powell, M. Barbieri, et al., Nature Chemistry 2, 106 (2010).
[3] S. Li, G. Long, F. Bai, and H. Zheng, PNAS 98, 11847 (2001).
[4] C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. DasSarma, Rev. Mod. Phys. 80, 1083 (2008).
[5] F. Wilczek, Nature Physics 5, 614 (2009).
[6] P. Zhang, K. Yaji, T. Hashimoto, Y. Ota, T. Kondo, K. Okazaki, Z. Wang, J. Wen, G. D. Gu, H. Ding, et al., Science 360, 182 (2018).
[7] L. Fu and C. L. Kane, Phys. Rev. Lett. 100, 096407 (2008).
[8] R. M. Lutchyn, J. D. Sau, and S. DasSarma, Phys. Rev. Lett. 105, 077001 (2010).
[9] J. P. Xu, C. Liu, M. X. Wang, J. Ge, Z. L. Liu, X. Yang, Y. Chen, Y. Liu, Z. A. Xu, C. L. Gao, et al., Phys. Rev. Lett. 112, 217001 (2014).
[10] J. P. Xu, M. X. Wang, Z. L. Liu, J. F. Ge, X. Yang, C. Liu, Z. A. Xu, D. Guan, C. L. Gao, D. Qian, et al., Phys. Rev. Lett. 114, 017001 (2015).
[11] A. Huang, A. D. Smith, M. Schwinn, Q. Lu, T. R. Chang, W. Xie, H. T. Jeng, and G. Bian, Phys. Rev. Materials 2, 054205 (2018).
[12] L. M. Schoop, L. S. Xie, R. Chen, Q. D. Gibson, S. H. Lapidus, I. Kimchi, M. Hirschberger, N. Hadolanaarachchige, M. N. Ali, C. A. Belvin, et al., Phys. Rev. B 91, 245147 (2015).
[13] Y. Xing, H. Wang, C. K. Li, X. Zhang, J. Liu, Y. Zhang, J. Luo, Z. Wang, Y. Wang, L. Ling, et al., npj Quantum Materials 1 (2016).
[14] S. Gupta, R. Juneja, R. Shinde, and A. K. Singh, Journal of Applied Physics 121, 214901 (2017).
[15] G. Bian, T. R. Chang, A. Huang, Y. Li, H. T. Jeng, D. J. Singh, R. J. Cava, and W. Xie, Phys. Rev. Materials 1, 021201 (2017).
[16] M. Kavitha, G. S. Priyanga, R. Rajeswarapalanichamy, and K. Iyakutti, Materials Chemistry and Physics 169, 71 (2016).
[17] H. M. Tutuncu, S. Bagci, S. P. Srivastava, and A. Akbulut, Journal of Physics: Condensed Matter 24, 455704 (2012).
[18] S. M. Schmucker, D. Clouser, T. J. Kraus, and B. M. Leonard, Dalton Transactions 46, 13524 (2017).
[19] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[20] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[21] X. Gonze, F. Jollet, F. A. Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J. M. Beeken, J. Bieder, A. Bokhanchuk, et al., Computer Physics Communications 205, 106 (2016).
[22] X. Gonze, B. Amadon, P. M. Anglade, J.-M. Beeken, F. Bottin, P. Boullanger, F. Bruneval, D. Caliste, R. Caracas, M. Ct, et al., Computer Physics Communications 180, 2582 (2009).
[23] X. Gonze, G. M. Rignanese, M. Verstraete, J. M. Beeken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, et al., Zeitschrift fr Kristallographie 220, 558 (2005).
[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[25] M. Torrent, F. Jollet, F. Bottin, G. Zrah, and X. Gonze, Computational Materials Science 42, 337 (2008).
[26] P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
[27] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[28] N. A. W. Holzwarth, A. R. Tackett, and G. E. Matthews, Computer Physics Communications 135, 329 (2001).
[29] C. G. Broyden, Math. Comp. 24, 365 (1970).
[30] R. Fletcher, The Computer Journal 13, 317 (1970).
[31] D. Goldfarb, Math. Comp. 24, 23 (1970).
[32] D. F. Shanno, Math. Comp. 24, 647 (1970).
[33] D. F. Shanno and P. C. Kettler, Math. Comp. 24, 657 (1970).
[34] D. Gresch, G. Autes, O. V. Yazyev, M. Troyer, D. Vanderbilt, B. A. Bernevig, and A. A. Soluyanov, Phys. Rev.
B 95, 075146 (2017).

[35] A. A. Soluyanov and D. Vanderbilt, Phys. Rev. B 83, 035108 (2011).

[36] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).

[37] K. Nakamura and M. Yashima, Materials Science and Engineering: B 148, 69 (2008).

[38] B. X. Liu and X. Y. Cheng, Journal of Physics: Condensed Matter 4, L265 (1992).

[39] E. K. Storms and N. H. Krikorian, J. Phys. Chem. 63, 1747 (1959).

[40] A. L. Bowman, The Journal of Physical Chemistry 65, 1596 (1961).

[41] J. Maibam, B. I. Sharma, R. Bhattacharjee, N. B. Singh, and R. K. Thapa, Assam University Journal of Science and Technology 6, 64 (2010).

[42] V. P. Zhukov and V. A. Gubanov, Journal of Physics and Chemistry of Solids 48, 187 (1987).

[43] A. Neckel, P. Rastl, R. Eibler, P. Weinberger, and K. Schwarz, Journal of Physics C: Solid State Physics 9, 579 (1975).

[44] J. Maibam, Ph.D. thesis, Assam University (2012).

[45] D. J. Singh and B. M. Klein, Physical Review B 46, 14969 (1992).

[46] T. Amriou, B. Boughafs, H. Aourag, B. Khelifa, S. Besson, and C. Mathieu, Physica B Condensed Matter 325, 46 (2003).

[47] B. I. Sharma, J. Maibam, R. S. Paul, K. Thapa, and R. K. Singh, Indian J. Phys. 84, 671 (2010).

[48] K. Schwarz, Journal of Physics C: Solid State Physics 8, 809 (1975).

[49] K. Schwarz, Journal of Physics C: Solid State Physics 10, 195 (1977).

[50] M. Sahnoun, C. Daul, M. Driz, J. C. Parlebas, and C. Demangeat, Computational materials science 33, 175 (2005).

[51] M. Sahnoun, C. Daul, J. C. Parlebas, C. Demangeat, and M. Driz, The European Physical Journal B-Condensed Matter and Complex Systems 44, 281 (2005).

[52] E. I. Isaev, S. I. Simak, I. A. Abrikosov, R. Ahuja, Y. K. Vekilov, M. I. Katsnelson, A. I. Lichtenstein, and B. Johansson, Journal of Applied Physics 101, 123519 (2007).

[53] J. Ma, M. Wu, Y. Du, S. Chen, J. Ye, and L. Jin, Materials Letters 63, 905 (2009).

[54] S. A. Hassanzadeh-Tabrizi, D. Davoodi, A. A. Beykzadeh, and A. Chami, International Journal of Refractory Metals and Hard Materials 51, 1 (2015).