Perovskite R3c phase AgCuF3: multiple Dirac cones, 100% spin polarization and its thermodynamic properties

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Abstract
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Keywords
agcu3:, phase, perovskite, dirac, cones, 100%, properties, spin, polarization, multiple, its, thermodynamic, r3c

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Very recently, experimentally synthesized $R\bar{3}c$ phase LaCuO$_3$ was studied by Zhang, Jiao, Kou, Liao & Du [J. Mater. Chem. C (2018), 6, 6132–6137], and they found that this material exhibits multiple Dirac cones in its non-spin-polarized electronic structure. Motivated by this study, the focus here is on a new $R\bar{3}c$ phase material, AgCuF$_3$, which has a combination of multiple Dirac cones and 100% spin polarization properties. Compared to the non-spin-polarized system LaCuO$_3$, the spin-polarized Dirac behavior in AgCuF$_3$ is intrinsic. The effects of on-site Coulomb interaction, uniform strain and spin–orbit coupling were added to examine the stability of its multiple Dirac cones and half-metallic behavior. Moreover, the thermodynamic properties under different temperatures and pressures were investigated, including the normalized volume, thermal volume expansion coefficient, heat capacity at constant volume and Debye temperature. The thermal stability and the phase stability of this material were also studied via ab initio molecular dynamic simulations and the formation energy of the material, respectively.

1. Introduction

What are the key challenges for the next generation of spintronics? Generations of researchers have faced this question as they worked toward a common goal: to realize dissipationless and ultra-high speed electron transmission (Awschalom & Flatté, 2007; Felser et al., 2016; Li & Yang, 2016). In order to obtain a non-dissipative spin current, the key is to find new materials with linear band crossing (i.e. Dirac cone characteristics) and high spin polarization near the Fermi level. To date, two new types of spintronic materials, i.e. Dirac spin-gapless semiconducting (DSGS) (Wang et al., 2018) material and Dirac half-metallic material, have been proposed. For Dirac half-metals (DHMs) (Ishizuka & Motome, 2012) there are novel Dirac cones in one spin channel and a gap in the other spin channel; therefore, the material theoretically exhibits 100% spin polarization. Unlike the non-spin-polarized Dirac structures in graphene and LaCuO$_3$ (Zhang et al., 2018), DHMs can break the time-reversal symmetry in spin-resolved orbital physics because of the differences in the orders of the charge current and spin current under time-reversal symmetry and the non-dissipative property of intrinsic coupling in Dirac half-metallic materials. DSGSs can be seen as an extreme situation of DHMs. It is
relatively difficult to realize DSGSs in the true sense, so a theoretical search for DHMs has become a necessary way to remove the bottleneck in spintronics.

DHMs were first proposed in triangular ferromagnets (Ishizuka & Motome, 2012). Since then, several materials have been theoretically proved to be two-dimensional (2D) DHMs (He et al., 2016; Liu et al., 2017); however, we found that in the current research, most 2D DHMs remain in the theoretical stage. A breakthrough was made in 2017, when Jiao et al. (2017) observed a new type of three-dimensional (3D) material, MnF₃, with R₃c symmetry; MnF₃ is a spin-polarized DHM, and, what is more, it has been prepared for many years. Thereafter, multiple Dirac cones were confirmed in R₃c-type LaMnO₃ (Ma et al., 2018), and this material has been fabricated for over 20 years (Norby et al., 1995). All of the above-mentioned works motivated us to find new Dirac materials with multiple Dirac cones around the Fermi level in the R₃c-type family. In 2018, an electronic structure calculation of R₃c-type LaCuO₃ was performed via first principles by Zhang et al. (2018), and multiple Dirac cones and an ultra-high Fermi velocity were also found in this topological Dirac semimetal. For LaCuO₃, two types of structures can be found that are related to oxygen pressure. The R₃c-type LaCuO₃ (Demazeau et al., 1972) was obtained at 1400°C and at a high oxygen pressure of ~5 GPa in 1972. Also, Jha et al. studied the structure-dependent phonon properties of LaMnO₃ (Talati & Jha, 2006a,b) by using a lattice dynamical simulation method based on the rigid ion model. However, LaCuO₃ is a non-spin-polarized system, which to a large extent limits its applicability to spintronics. All these findings motivated us to find new Dirac materials with multiple Dirac cones around the Fermi level and full spin polarization in the R₃c-type family.

On the other hand, a material with multiple Dirac cones has a stronger nonlinear electromagnetic response than a material with a single Dirac cone. Furthermore, materials with multiple Dirac cones have received extensive attention from researchers recently. In 2012, Malko et al. predicted via first principles a new 6,6,12-graphyne which features two self-doped nonequivalent distorted Dirac cones (Malko et al., 2012). Their results also reflect electronic properties of 6,6,12-graphyne that are even more fascinating than those of graphene. In 2015, Liu et al. studied the electronic and magnetic properties of a germanene layer on an Al (111) surface, and they found that this new system exhibited multiple Dirac cones (Liu et al., 2015). To be more specific, they found two Dirac points at high-symmetry k and k’ points and three Dirac points on the k(k’)−m high-symmetry lines. Xu et al. (2014) predicted that S-graphene exhibits four Dirac points in its first Brillouin zone; however, only two of these points are independent due to the symmetry relation. As far as we know, almost all of this research focuses on 2D materials.

In this manuscript, we focus on a new 3D R₃c-type material, AgCuF₃, and we study its electronic structure, magnetic and thermodynamic properties according to first-principles methods and the quasi-harmonic Debye model. Moreover, a uniform strain effect was added in this system, and the calculated results show that the half-metallic properties and multiple Dirac cones of this system are very robust. For the spin–orbit coupling effect, the multiple Dirac cones near the Fermi level show strong resistance, reflecting that such a material exhibits a long spin coherence length. Compared to the non-spin-polarized system LaCuO₃, the spin-polarized Dirac behavior in AgCuF₃ is intrinsic and does not need the help of additional experimental conditions such as applied electric field and pressure.

2. Computational methods
In this work, all the calculations of the electronic structures were performed by means of density functional theory as implemented in the VASP (Vienna ab initio simulation package) code (Kresse & Joubert, 1999; Kresse & Hafner, 1993). The exchange and correlation functionals were described by the Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996) parameterization of GGA (Ernzerhof & Scuseria, 1999). The projector augmented wave (Bloch, 1994) was selected to deal with the interaction between the ion cores and valence electrons. An energy cutoff of 500 eV was employed in the plane wave basis set. The unit cell was optimized until the force and total energies were less than 0.005 eV Å⁻¹ and 0.0000001 eV, respectively. We should point out that, in this work, all structural parameters (lattice constants and free ionic positions) were optimized (Gupta et al., 2013; Gupta & Jha, 2014; Karki et al., 1997). The thermodynamic properties of this system were calculated based on the quasi-harmonic Debye model. In this work, the spin–orbit coupling effect was also added to examine the band structures of AgCuF₃. The thermodynamic stability of a 2 × 2 × 1 superlattice AgCuF₃ was tested via ab initio molecular dynamics simulations (AIMD) at 300 K in the framework of the Nosé–Hoover thermostat ensemble. Also, the DFT+U method was selected to better describe the strong correlation effect for d electrons and to examine the electronic structures of AgCuF₃.

3. Results and discussion
The perovskite (R₃c)-type AgCuF₃ crystal structures are shown in Fig. 1; the structure contains Cu-centered octahedrals, and its optimized lattice constants are a = b = 5.674 Å and c = 13.754 Å. To search for the most stable magnetic structures, we considered a 1 × 1 × 1 unit cell and a 1 × 1 × 2 superlattice to carry out the total energy calculations. The diagrams of both are shown in Fig. S1.

For systematically evaluating the ground-state magnetic structures of AgCuF₃, we set ferromagnetic (FM), non-magnetic (NM) and antiferromagnetic (AFM) orderings as shown in Figs. S1(a)–S1(d). In particular, there are two different kinds of AFM states in our models for generally examining the dependence between magnetic structures and energy stability. The energy difference between FM ordering and the other orderings is defined as ΔE_{NM/AFM} = E_{NM/AFM} – E_{FM}. For the conventional cell, ΔE_{NM}, ΔE_{AFM1} and ΔE_{AFM2} are +85, +6 and +93 meV, respectively. Our results clearly show that the FM ground state is the most stable magnetic
state for the AgCuF₃ material. In order to obtain a more
general result, we calculated continuously the magnetic
structure of the above-mentioned 1 × 1 × 2 superlattice as
shown in Figs. S1(e)–S1(g). Here, the FM, AFM and NM states
were also considered. The results show that Δₕₑ and
Δₐₑ are +160 meV and +27 meV, respectively. According
to our computation, it can be seen that the FM state is always
the most energetically favorable magnetic configuration rela-
tive to the NM or AFM states as shown by the considerable
energy differences. For the FM state of AgCuF₃, the total
magnetic moment value was calculated to be ~6 μₜ per unit
cell, and the magnetic moments are mainly distributed around
six Cu atoms (~0.72 μₜ per Cu atom). The atomic magnetic
moments of the Ag and F atoms are about 0.01 μₜ and
0.085 μₜ, respectively.

We calculated the electronic structures on the basis of the
FM state for AgCuF₃. In Fig. 2, one can see that there are
multiple linear dispersion band crossings (see the yellow areas
in Fig. 2) around the Fermi level in the spin-down channel.
Normally, there is one cone at the highly symmetric A-point,
one along the A–H line, two along the K–G line, four along

(a)

(b)

(c)

Figure 1
Three views of crystal structures of three perovskite (R₃c) AgCuF₃ unit
cells. The gray balls represent Ag, the red balls represent Cu and the
green balls represent F.

Figure 2
(a) Calculated spin-up band structures of R₃c AgCuF₃ with its first
Brillouin zone (spin up). As shown in insert map of (a), the high-
symmetry points G-A-H-K-G-M-L-H in the first Brillouin zone are
selected. (b) Calculated spin-down band structures of R₃c AgCuF₃. Dirac
cones are distinguished by different numbers. Dirac cones near the Fermi
level are shown by yellow squares and Dirac-like crossings in the region
far from the Fermi level are represented by purple squares. (c) Total
density of states of the R₃c AgCuF₃ material.
the G–M line and two along the M–L line. Our results are in good agreement with the results of A. J. Du’s team (Ma et al., 2018). It is noteworthy that there are also some Dirac-like crossings (see the purple areas above and below the Fermi level) located in the region far from the Fermi level. In addition, although three cones open small gaps owing to Pauli repulsion, the possible valleytronic features (Lensky et al., 2015) of gaped Dirac cones could be further investigated. Moreover, as Zhang et al. (2018) reported, we also found that the crossing bands at cones 1–8 and 10 have opposite signs, reflecting that these points are type I Dirac points. However, cone 9 has the same sign, thus indicating that this point is a novel type II Dirac point, also named a distorted Dirac point. Due to the spin-down channel band structures being highly consistent with those of LaCuO$_3$ (Zhang et al., 2018), we can judge it in the same way and conclude that these Dirac cones near the Fermi level are protected by the $D_{3d}$ symmetry. The GGA+U method was also taken into consideration in this work; the band structures in both spin channels under different $U$ values were calculated and the results can be found in Fig. S2 ($U = 4$ eV for Cu-$3d$ orbit) (Awschalom & Flatté, 2007) and Fig. S3 ($U = 4$ eV for Cu-$3d$ orbit and Ag-$4d$ orbit). From the results, we can see that no matter how the $U$ value changes, the multiple linear band dispersions and the half-metallic properties of AgCuF$_3$ hardly change.

In the spin-up channel, a large semiconductor-like ($\sim 1.25$ eV) band gap occurs in the total density of states (TDOS) (see Fig. 2), ensuring a half-metallic property. To further confirm the physical origin of the novel electronic behavior of the material, the orbital-resolved band structures and projected density of states (PDOS) in the spin-down channel are given in Fig. 3. Near the Fermi level, combining the above-mentioned two kinds of spectra, we can clearly see that the Dirac cones are mainly dominated by the $3d$-orbits of Cu atoms, whereas the $4d$-orbits of Ag atoms are localized in the range of $-1.5$ eV to $-0.5$ eV and the $2p$-orbits of F atoms are mainly localized below $-3$ eV. However, for the Dirac cones in the range of $0 \sim 0.2$ eV, the hybridization between the $2p$-orbitals of fluorine and the $3d$-orbitals of Cu atoms cannot be ignored. On the other hand, considering the criterion for

Figure 3
Orbital-resolved band structures for AgCuF$_3$ contributed by the (a) Ag-$d$, (b) Cu-$d$, and (c) F-$p$ orbits. Thicker lines indicate a higher contribution, while thinner lines mean a lower contribution. (d) Projected density of states of the $R3c$ AgCuF$_3$ material.
Stoner ferromagnetism, the high density of states of majority spin $N_{\uparrow}$ near the Fermi level reduces the kinetic energy increment in the spin-flip and is thus beneficial to the formation of its FM ground state. The general spin polarization ratio can be estimated as $\rho = |\rho_\uparrow - \rho_\downarrow|/|\rho_\uparrow + \rho_\downarrow|$, in which $\rho_\uparrow$ and $\rho_\downarrow$ represent the spin-up states and spin-down states, respectively, extracted from the TDOS spectrum. AgCuF$_3$ possesses 100% spin polarization, which is important if it is to be used to generate a fully spin-polarized current for next-generation spintronic device applications (Wang et al., 2017).

In many Dirac materials, such as graphene, germanene (Dávila & Le Lay, 2016) and silicene (Zhao et al., 2016), their symmetry-protected Dirac states are mainly composed of $p$-orbitals with small spin–orbit coupling (SOC), while those in AgCuF$_3$ are derived from $d$-orbits with stronger SOC. Generally, the SOC effect can open a gap between the Dirac cones, as has been theoretically and experimentally confirmed (Blanco et al., 2004; Min et al., 2006; Yao et al., 2007), and many Dirac materials are thus formally a topological insulator, though their gaps are extremely small in practice. It is natural to search for the Dirac states which are robust against SOC.

Here, to evaluate the stability of the AgCuF$_3$ Dirac states, we consider the SOC effect to calculate its band structures, as shown in Fig. S4. Interestingly, the $D_{3d}$ symmetry-protected Dirac cones are not affected, indicating a long spin coherence length for future spin-transport devices. The stability of the electronic structure under uniform strain was also examined, as shown in Fig. 4. We exerted compressed and expansive uniform strain from $-8$ GPa to +4 GPa on a relaxed AgCuF$_3$ lattice. Some cones opened vanishingly small gaps, while the other cones remained intact. This also strongly proves that such multiple Dirac cones are robust enough to withstand mechanical impact.

We carried out spin-polarized ab initio molecular dynamics simulations (AIMD) of a $2 \times 2 \times 1$ superlattice with a Nosé–Hoover thermostat at 300 K for 5 ps, as shown in Fig. 5(c). During the simulation, the total energy was almost invariant with respect to time; moreover, the geometric configuration did not suffer obvious disturbance in Figs. 5(a) and 5(b), indicating the room-temperature stability of the AgCuF$_3$ crystal. The formation energy of $R\bar{3}c$ AgCuF$_3$ (FM state) was calculated and results of $E(f)$ are listed in Table S1. The results

![Figure 4](image-url)

Figure 4
Band structures of AgCuF$_3$ with the effect of uniform strain: (a and c) spin-up channel; (b and d) spin-down channel.
of \( E(f) \) are all smaller than 0 eV, reflecting that AgCuF\(_3\) is structurally stable. Further, according to the obtained \( E(f) \), this material may be synthesized experimentally (Li et al., 2018).

Furthermore, to understand the thermodynamic behavior of the material under widely constrained circumstances, such as high temperature and high pressure, we calculated a series of thermodynamic parameters: coefficient of thermal volume expansion \( \alpha V \), heat capacity \( C_V \) and Debye temperature \( \theta_D \). With respect to the quasi-harmonic Debye model, the thermodynamic behaviors were confirmed in the temperature range 0–2000 K with respect to the pressure range 0–40 GPa.

More details about the quasi-harmonic Debye model can be found in the supporting information.

Fig. S5(a) shows the rate of variation with respect to pressure at some fixed constant temperatures, while Fig. S5(b) shows the variation of the normalized \( V/V_0 \) with respect to temperature under some fixed constant pressure values; here, \( V_0 \) is the initial volume, while \( V \) denotes the volume under pressure/temperature. With pressure increasing at a constant temperature, the rate displays a strong negative linear dependency; also, the corresponding slope in Fig. S5(a) is higher under high temperature than it is under low temperature. On the other hand, the rate shows a strong positive linear dependency with increasing temperature at constant pressure, and the corresponding slope in Fig. S5(b) decreases under higher pressure.

The \( \alpha V \) value plays an important role in the theoretical prediction of thermal equations-of-state and in the understanding of thermodynamic properties in experimental studies. We plotted \( \alpha V \) as a function of temperature and pressure as we did for \( V/V_0 \). Under a given pressure, in Fig. S6(a), \( \alpha V \) sharply increases with increasing temperature up to \( \sim 300 \) K and becomes slower after that. Considering the impact from the pressure, higher pressure restrains the increase in \( \alpha V \). In Fig. S6(b), for a given temperature, \( \alpha V \) gradually decreases with increasing pressure, while a higher temperature does not affect its variational tendency but elevates its initial value. In practical situations, we mainly pay attention to the value under 300 K and 0 GPa. Under 300 K and 0 GPa conditions, \( \alpha V \) of AgCuF\(_3\) is about \( 1.37 \times 10^{-5} \) K\(^{-1}\).

We further calculated the expected variation of the heat capacity \( C_V \), which can reveal the vibrational properties of the system. In Fig. S7(a), \( C_V \) is plotted as a function of temperature for different given pressures. One can see that \( C_V \) increases steeply with increasing temperature up to 300 K; after that, it slowly increases until it reaches the Dulong–Petit limit, indicating that thermal energy at high temperature excites all phonon modes. Clearly, variation of the pressure has little impact on the \( C_V–T \) curve; overall, change in \( C_V \) is slower under high pressure. For Fig. S7(b), we fixed the temperature to plot the \( C_V–P \) curve. The overall trend of variation of \( C_V \) is decreasing with increasing pressure. Furthermore, the initial value of the \( C_V–P \) curve increases under higher pressure, while the slope is diminished. Under 300 K and 0 GPa conditions, a general \( C_V \) value is about 92 J mol\(^{-1}\) K\(^{-1}\).

The Debye temperature \( \theta_D \) is strongly associated with thermal properties in a solid, such as heat capacity, elastic behavior and so on. Fig. S8 displays the \( \theta_D–T \) relation for a given pressure and the \( \theta_D–P \) relation for a given temperature. \( \theta_D \) possesses a negative quasi-linear dependency with respect to temperature. In a high-pressure environment, the initial value of \( \theta_D \) can be promoted and its decreasing trend can be restrained to some extent. Moreover, \( \theta_D \) shows a positive quasi-linear dependency with respect to pressure. The \( \theta_D–P \) curve indicates that high temperatures are favorable to the \( \theta_D \) increase. In our calculation, \( \theta_D \) under 300 K and 0 GPa conditions was found to be equal to \( \sim 750 \) K.
Our calculations display the excellent thermodynamic properties of AgCuF₃. We hope our results can provide helpful references to support future experimental work with perovskite AgCuF₃.

4. Conclusions
We proposed a theoretical investigation of perovskite R₃c phase AgCuF₃, which possesses multiple Dirac cones, 100% spin polarization and excellent thermodynamic properties, using first-principles calculations and a quasi-harmonic Debye model. Its excellent electronic structures are robust enough against on-site Coulomb interaction, uniform strain and the SOC effect; also, its thermodynamic stability and phase stability were examined via AIMD and formation energy. Overall, perovskite R₃c phase AgCuF₃ can be seen as a promising candidate for applications in future spintronic devices. We hope our work can provide guidance for future experimental investigations.

5. Related literature

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References