Persistent exchange splitting in the chiral helimagnet Cr$_{1/3}$NbS$_2$

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(Received 23 February 2022; revised 4 May 2022; accepted 29 June 2022; published 18 July 2022)

Using high-resolution angle-resolved photoemission spectroscopy and ab initio calculation, we systematically investigate the electronic structure of the chiral helimagnet Cr$_{1/3}$NbS$_2$ and its temperature evolution. The comparison with NbS$_2$ suggests that the electronic structure of Cr$_{1/3}$NbS$_2$ is strongly modified by the intercalation of Cr atoms. Our ab initio calculation, consistent with experimental results, suggests strong hybridization between Nb- and Cr-derived states near the Fermi level. In the chiral helimagnetic state (below the Curie temperature, $T_c$), we observe exchange splitting of the energy bands crossing the Fermi level, which follows the temperature evolution of the magnetic moment, suggesting a strong interaction between the conduction electrons and Cr spin moments. Interestingly, the exchange splitting persists far above $T_c$ with weak temperature dependence, in drastic contrast to the itinerant ferromagnetism described by the Stoner model, indicating the existence of short-range magnetic order. Our results provide important insights into the interplay between the electronic structure and magnetism in Cr$_{1/3}$NbS$_2$, which is helpful for understanding the microscopic mechanism of chiral helimagnetic ordering.

DOI: 10.1103/PhysRevB.106.035129

I. INTRODUCTION

Chiral materials lacking both inversion and mirror symmetries exhibit many interesting properties, such as chiral Weyl fermions and extremely long Fermi arcs [1–6], a quantized circular photogalvanic current [7], and a chiral magnetic effect [8]. Particularly, if a chiral material hosts magnetic ordering, the competition between the ferromagnetic (FM) exchange interaction and the Dzyaloshinskii–Moriya interaction (DMI) can result in helical alignment of spins, forming the so-called chiral helimagnet (CHM). CHMs can harbor novel topological excitation with magnetic vortices known as skyrmions that can be effectively tuned by external magnetic field or spin-polarized electrical currents [9–12], promising great application potential for spintronic devices. So far, CHM materials have been discovered in mainly two space groups: cubic space group P2$_1$3, such as MnSi [9,13], Fe$_{1-x}$Co$_x$Si [14,15], FeGe [16–18], Cu$_2$OSeO$_3$ [19,20]; and cubic space group P4$_1$32 or P4$_2$32, such as $\beta$-Mn-type Co-Zn-Mn [21] and FePtMo$_3$N [22].

Among the CHMs, Cr$_{1/3}$NbS$_2$ is unique since it hosts a one-dimensional chiral soliton lattice instead of two-dimensional or three-dimensional skyrmions [23]. It crystalizes in a layered hexagonal structure with the space group of P6$_3$22. Within each unit cell, there are two trigonal prismatic NbS$_2$ layers that are rotated by 180° with respect to each other. The Cr atoms occupy the octahedral holes between two adjacent NbS$_2$ layers and order in a (√3×√3R30°) superstructure. Cr$_{1/3}$NbS$_2$ can therefore be considered as Cr-intercalated 2H-NbS$_2$ [Fig. 1(a)]. Below about 125 K, the intercalated Cr atoms with a local spin moment of about 3 $\mu_B$ order ferromagnetically and the system enters into a helimagnetic ground state with a large helix period of 48 nm along the chiral c-axis [Fig. 1(b)]. The difference in the magnetic moment measured under field cooling (FC) and zero field cooling (ZFC) conditions in Fig. 1(c) suggests a ferromagnetic transition in Cr$_{1/3}$NbS$_2$. When an external magnetic field is applied perpendicular to the c-axis, a highly tunable and robust chiral soliton lattice can be observed [23], indicating the important application potential in spintronic devices.

Despite extensive research effort, the microscopic mechanism of the CHM ordering in Cr$_{1/3}$NbS$_2$ is still controversial. According to conventional understanding of magnetically intercalated transition metal dichalcogenides, the FM exchange interaction between Cr ions has a Ruderman–Kittel–Kasuya–Yosida (RKKY) form that is mediated by the itinerant Nb conduction electrons [24,25]. In this scenario, the local
orbitals of Cr ions contribute negligibly to the Fermi surface (FS) of Cr$_{1/3}$NbS$_2$, but only dope electrons to the system. However, this picture has been challenged by recent experimental [26] and theoretical [24,26,27] results, which suggest a significant contribution of Cr ions to the density of states near the Fermi level ($E_F$). Indeed, previous angle-resolved photoemission spectroscopy (ARPES) experiments show strong hybridization between Nb- and Cr-derived electronic states near $E_F$ [28,29], and a Hund’s exchange interaction—instead of the RKKY interaction—between Cr ions has been proposed [29]. To understand the mechanism of the novel magnetic ordering, it is essential to study adequately the electronic structure and its interplay with the magnetism of Cr$_{1/3}$NbS$_2$.

In this work, we systematically study the electronic structure of Cr$_{1/3}$NbS$_2$ and its temperature evolution using high-resolution ARPES. We reveal a drastic difference between the electronic structures of NbS$_2$ and Cr$_{1/3}$NbS$_2$, consistent with our ab initio calculation that suggests strong hybridization between Cr- and Nb-derived states near $E_F$. In the CHM state, we observe exchange splitting of energy bands crossing $E_F$, with a magnitude that nicely follows the temperature evolution of the magnetic moment below the Curie temperature $T_c$, indicating strong coupling between itinerant conduction electrons and Cr spin moments. Interestingly, the exchange splitting persists even at temperatures far above $T_c$, in drastic contrast to the itinerant FM described by the Stoner model. Our results suggest an important role of short-range magnetic interaction in Cr$_{1/3}$NbS$_2$, which will help understand the interplay between the electronic structure and magnetism in the system.

II. METHODS

The Cr$_{1/3}$NbS$_2$ crystals were grown via employing the chemical vapor transport method by using iodine as the
transfer agent. Stoichiometric Cr powder (99.9%, Adamas), Nb powder (99.95%, Aladdin), and S powder (99.9%, Adamas) were mixed and ground in a mortar. Then the mixture was sealed in a quartz tube together with the iodine in a vacuum of $10^{-4}$ Pa. The assembly was placed into a single temperature-zone tube furnace and the temperature of the high-temperature region was kept at 1000 °C. After two weeks, large crystals of Cr$_{1/3}$NbS$_2$ were obtained at the cold end of the quartz tube. The crystallographic phase and crystal quality examinations of Cr$_{1/3}$NbS$_2$ were performed on a single-crystal x-ray diffractometer equipped with a Mo Kα radioactive source ($\lambda = 0.71073$ Å). The diffraction patterns could be satisfyingly indexed on the basis of a Nb$_3$CoS$_6$ polytype structure (space group: P6$_3$22, No. 182) with the lattice parameters $a = b = 5.74$ Å, $c = 12.09$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$.

High-resolution ARPES measurements were performed at beamline 13U of National Synchrotron Radiation Laboratory (NSRL), beamlines 4.0.3 and 10.0.1 of Advanced Light Source (ALS), and beamline 5-4 of Stanford Synchrotron Radiation Light Source (SSRL). Data were collected with a Scienta R4000 (DA30) electron analyzer at NSRL and ALS (SSRL). The overall energy and angular resolutions were set to 15 meV and 0.2°, respectively. The samples were cleaved in situ and measured under ultra-high vacuum less than $1.0 \times 10^{-10}$ mbar.

First-principles band structure calculations were performed using the QUANTUM ESPRESSO code package [30] for the nonmagnetic calculations and the Vienna ab initio simulation package (VASP) [31] for the magnetic calculations with plane-wave basis. The exchange–correlation energy was considered under a Perdew–Burke–Ernzerhof-type generalized gradient approximation (GGA) [32]. For the calculation of Cr$_{1/3}$NbS$_2$, the GGA + U method was applied to describe the 3d-orbitals of Cr atoms, where on-site Coulomb interaction U was set to 4 eV. Spin-orbit coupling was not included due to its minor effect on band structure. Experimental lattice parameters were used. The cutoff energy for the plane-wave basis was set to 480 eV for calculations with QUANTUM ESPRESSO and 400 eV for calculations with VASP. A Γ-centered Monkhorst–Pack k-point mesh of $9 \times 9 \times 4$ with a spacing of 0.15 Å$^{-1}$ was adopted in all self-consistent calculations.

### III. RESULTS AND DISCUSSIONS

Figure 2 shows the comparative study of the electronic structure of NbS$_2$ and Cr$_{1/3}$NbS$_2$. On the FS of NbS$_2$, we observe a large hole pocket around the $\bar{\Gamma}$ and $\bar{K}$ points, respectively [Fig. 2(a)]. We do not observe the band splitting caused by the coupling between the two NbS$_2$ layers in one unit cell [33]. In Cr$_{1/3}$NbS$_2$, by contrast, we observe an extra small hole pocket around the $\bar{\Gamma}$ point [Fig. 2(b)]. Due to the $(\sqrt{3} \times \sqrt{3})R(30^\circ)$ superstructure, the Brillouin zone (BZ) of Cr$_{1/3}$NbS$_2$ is rotated by 30° and shrinks by 2/3, compared to the BZ of NbS$_2$. Along $\bar{\Gamma}K$ and $\bar{\Gamma}M$, we observe only one band crossing $E_F$ in NbS$_2$, while there are two bands, marked as $\beta$ and $\gamma$, crossing $E_F$ along $\bar{\Gamma}K\bar{M}$ and $\bar{\Gamma}\bar{M}\bar{\Gamma}$ in Cr$_{1/3}$NbS$_2$. 

FIG. 3. (a)–(h) Band structure of Cr$_{1/3}$NbS$_2$ along $\bar{\Gamma}\bar{M}$ measured at selected photon energies. Data were measured at 20 K.
Figure 3(a)–3(h) shows the band structure of Cr\textsubscript{1/3}NbS\textsubscript{2} measured with different photon energies, which can measure the $k_z$ dispersion of energy bands and reflects the interlayer coupling. Both the \(\beta\) and \(\gamma\) bands show weak $k_z$ dependence, except that the spectral weight of the \(\gamma\) band is enhanced at high photon energies due to the matrix element effect. We observe an extra \(\alpha\) band with its band top touching \(E_F\). It shows a continuum-like spectral weight distribution, suggesting its strong $k_z$ dispersion, similar to the \(\alpha\) band in NbS\textsubscript{2} [Fig. 2(c)]. Apparently, the electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2} cannot be derived from a rigid shift of the electronic structure of NbS\textsubscript{2} induced by electron donation from Cr ions. Although the overall dispersion of the \(\alpha\) and \(\gamma\) bands are very similar in NbS\textsubscript{2} and Cr\textsubscript{1/3}NbS\textsubscript{2}, their relative energy positions are different. The \(\alpha\) band shifts toward \(E_F\) for about 250 meV, while the \(\gamma\) band shifts toward higher binding energies for about 100 meV in Cr\textsubscript{1/3}NbS\textsubscript{2}. Therefore, the electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2} cannot be derived from electron doping in NbS\textsubscript{2} by Cr intercalation. Moreover, the $k_z$ dispersion of the \(\alpha\) band also suggests an important role of interlayer coupling in the electronic structure and magnetic properties of Cr\textsubscript{1/3}NbS\textsubscript{2}.

To understand further the influence of Cr atoms on the electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2}, we perform an \textit{ab initio} calculation on the electronic structures of NbS\textsubscript{2} and Cr\textsubscript{1/3}NbS\textsubscript{2}, as illustrated in Fig. 4. For better comparison, the result of NbS\textsubscript{2} is artificially folded into a \((\sqrt{3} \times \sqrt{3})R(30')\) superstructured BZ similar to that of Cr\textsubscript{1/3}NbS\textsubscript{2}. Figure 4(a) and 4(b) compares the electronic structures of NbS\textsubscript{2} and paramagnetic Cr\textsubscript{1/3}NbS\textsubscript{2} (on site Coulomb interaction \(U = 4\) eV). Apparently, the electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2} cannot be understood by electron doping from intercalated Cr ions. Rather, the number of energy bands crossing \(E_F\) increases due to the hybridization between the Cr- and Nb-derived states, consistent with our experiment in Fig. 2. In the FM state, we observe spin-splitting of the energy bands due to the exchange interaction [Fig. 4(c)]. In Fig. 4(d), we compare the calculated electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2} in the CHM and FM states. No noticeable difference is observed, suggesting the same influence of the CHM and FM ordering on the electronic structure, which is reasonable considering the large helix period of the CHM state [24,26,27]. Therefore, the DMI that is responsible for the spiral spin ordering serves as a weak perturbation to the FM state [26]. Figure 4(e) shows the orbital-projected calculation of the electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2} in the FM state. We observe a substantial spectral weight of Cr $d$-orbitals near \(E_F\), confirming the strong hybridization between the Cr- and Nb-derived states, consistent with previous \textit{ab initio} calculations [24,26,27].

Both our experiments and calculations are in good agreement with previous results. Nevertheless, it is noteworthy that due to the electronic correlation of Cr $d$-states, the multiband nature of the system, and complicated magnetic ordering, there still exist clear deviations between the ARPES measured and calculated electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2} [24,26–29]. For example, in the FM state, there are more bands crossing \(E_F\) in the calculation, and some calculated bands are missing in the experiments (Supplemental Materials Fig. S2 [34]). Further experimental and theoretical investigations are highly demanded to understand fully the electronic structure of Cr\textsubscript{1/3}NbS\textsubscript{2}.

Figure 5 tracks the temperature evolution of the band structure of Cr\textsubscript{1/3}NbS\textsubscript{2} measured with improved energy resolution using relatively low photon energy. Figure 5(a)–5(e) show ARPES intensity maps at selected temperatures. In the CHM state at 15 K, we observe four bands near \(E_F\), marked as \(\alpha\), \(\beta_1\), \(\beta_2\), and \(\gamma\) in Fig. 5(a), compared to the two bands \(\beta\) and \(\gamma\) in Fig. 2. With increasing temperature, the splitting between \(\beta_1\) and \(\beta_2\) gradually decreases and can hardly be resolved at 195 K. To quantify the evolution of the band structure, we collect the momentum distribution curves (MDCs) at \(E_F\) taken at different temperatures [Fig. 5(f)] and fit each MDC to multiple Lorentzians. The extracted Fermi crossings of the \(\beta_1\), \(\beta_2\), and \(\gamma\) bands are overlaid on the false-color plot of the MDCs in Fig. 5(g). The \(\beta_1\) and \(\beta_2\) bands approach each other with increased temperature, with a sudden change of their splitting.
near 125 K, where the \( \gamma \) band also shows a sudden change of its position. From the temperature evolution of the energy bands, we conclude that the FM ordering strongly influences the band structure of Cr\(_{1/3}\)NbS\(_2\), and the splitting between the \( \beta_1 \) and \( \beta_2 \) bands is the exchange splitting caused by the FM ordering.

In general, as described by the Stoner model, if the long-range FM order is mainly contributed by the itinerant electron around \( E_F \), the magnitude of exchange splitting in metallic FM materials is proportional to the magnetic moment and becomes zero above \( T_c \). In Fig. 5(h), we compare the temperature evolution of the exchange splitting and the magnetic moment. Below \( T_c \), the exchange splitting follows the increasing magnetic moment with decreasing temperature, suggesting a strong interplay between the conduction carriers and the magnetic moment of the system. Above \( T_c \), interestingly, the exchange splitting deviates from the magnetic moment curve and persists up to at least 195 K [Fig. 5(g) and 5(h)], in drastic contrast to the Stoner model, suggesting that Cr\(_{1/3}\)NbS\(_2\) is not a band magnetic material.

The exchange splitting that is persistent above \( T_c \) has been widely observed in metallic ferromagnets, including Fe, Ni, SrRuO\(_3\), and Fe\(_3\)GeTe\(_2\) [35–40], despite the controversial experimental results in Ni [41]. However, the temperature dependence of the exchange splitting is quite different in these materials. In SrRuO\(_3\) and Fe\(_3\)GeTe\(_2\), the bands stay put with increasing temperature, suggesting a minor impact of long-range magnetic ordering on the exchange splitting [38,39], consistent with a localized intra-atomic exchange interaction [35]. By contrast, the exchange splitting in Cr\(_{1/3}\)NbS\(_2\) strictly follows the magnetic moment below \( T_c \), but shows minor temperature dependence above \( T_c \). We emphasize that, despite the helimagnetic nature of Cr\(_{1/3}\)NbS\(_2\), the exchange splitting is mainly induced by the FM order in the system [Fig. 4(d)] [26]. Therefore, similar to the previous result in Ni [35], the observed temperature evolution of the exchange splitting may be understood within the Oguchi model that describes short-range order by exactly treating the interactions between neighboring magnetic ion pairs while approximating the other pairs with a mean field [35]. Consistently, previous measurements of critical exponents support the short-range magnetic coupling between Cr atoms [42,43]. On the other hand, the persistent exchange splitting above \( T_c \) can also be induced by the formation of short-range FM order, such as the Griffith phase, in which finite-size FM clusters exist in the paramagnetic phase at high temperatures [44]. Further detailed experimental and theoretical works are required to understand fully the observed exchange splitting at temperatures far above \( T_c \).
IV. CONCLUSION

In conclusion, we have systematically investigated the electronic structure of the CHM Cr$_{1/3}$NbS$_2$ and its temperature evolution. Both experimental results and \textit{ab initio} calculations show strong hybridization between the Cr- and Nb-derived states near $E_F$, in contrast to a simple Cr-doping rigid-shift scenario. Moreover, we observed exchange splitting of the band structure that persists far above $T_c$, which is beyond expectation of a band magnetism and suggests the existence of short-range magnetic order in Cr$_{1/3}$NbS$_2$. Our results provide important insight into the understanding of the electronic and magnetic properties of the monox axis CHM Cr$_{1/3}$NbS$_2$.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants No. 11774190, No. 11427903, No. 11634009), the National Key R&D Program of China (Grants No. 2017YFA0304600, No. 2017YFA0305400, and No. 2017YFA0402900), and EPSRC Platform Grant (Grant No. EP/M020517/1). Use of the Stanford Synchrotron Radiation Light Source, SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. This research used resources of the Advanced Light Source, a US Department of Energy Office of Science User Facility under Contract No. DE-AC02-05CH11231.
[34] See Supplemental Materials at http://link.aps.org/supplemental/10.1103/PhysRevB.106.035129 for (i) details about the fit of energy distribution curves (EDCs) and MDCs, (ii) comparison between the experimental and calculated band structures near the Fermi level, and (iii) the calculated band structure of Cr1/3NbS2 with different Coulomb interaction between Cr atoms, which includes Refs. [45–47].