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SPECIAL TOPIC — Superconductivity in vanadium-based kagome materials

Surface-induced orbital-selective band reconstruction in kagome superconductor CsV_3Sb_5

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The two-dimensional (2D) kagome superconductor CsV_3Sb_5 has attracted much recent attention due to the coexistence of superconductivity, charge orders, topology and kagome physics, which manifest themselves as distinct electronic structures in both bulk and surface states of the material. An interesting next step is to manipulate the electronic states in this system. Here, we report angle-resolved photoemission spectroscopy (ARPES) evidence for a surface-induced orbital-selective band reconstruction in CsV_3Sb_5. A significant energy shift of the electron-like band around Γ and a moderate energy shift of the hole-like band around M are observed as a function of time. This evolution is reproduced in a much shorter time scale by *in-situ* annealing of the CsV_3Sb_5 sample. Orbital-resolved density functional theory (DFT) calculations reveal that the momentum-dependent band reconstruction is associated with different orbitals for the bands around Γ and M, and the time-dependent evolution points to the change of sample surface that is likely caused by the formation of Cs vacancies on the surface. Our results indicate the possibility of orbital-selective control of the band structure via surface modification, which may open a new avenue for manipulating exotic phenomena in this material system, including superconductivity.

Keywords: photoemission, kagome superconductor, band structure

PACS: 74.25.Jb, 74.70.−b, 79.60.−i, 74.20.Pq **DOI:** 10.1088/1674-1056/ac4f50

1. Introduction

Due to the exotic lattice geometry, kagome materials provide a novel platform to explore various intriguing quantum phenomena.[1–7] Recently, a new family of kagome metals AV_3Sb_5 (A = K, Rb and Cs) has been discovered.[7–10] Superconductivity,[7–9,11–15] charge density wave,[7,8,16–21] pair density wave[21] and non-trivial topology[7,22,23] have all been reported in this family of materials. Distinct electronic structures have also been revealed in both bulk and surface states of the materials,[23–33] which successfully accommodate various novel phenomena in this material system. An exciting next step is to manipulate the associated electronic states, which would not only help understand the origin of mysterious physical interactions but also open a new window for exploring emergent quantum phenomena.

In this paper, we unveil the electronic band structure of CsV_3Sb_5 via systematic ARPES measurements and report the discovery of a distinct momentum-dependent band evolution as a function of time. A significant energy shift of the electron-like band around Γ is observed while only a moderate energy shift of the hole-like band around M is revealed. This phenomenon is reproduced in a much shorter time scale by *in-situ* annealing the CsV_3Sb_5 sample. Orbital-resolved density functional theory (DFT) calculations show different orbital characters for the bands around Γ and M respectively, which indicates an orbital-selective band reconstruction. Through careful analysis, we attribute this time- and momentum-dependent band reconstruction to the formation of Cs vacancies on the sample surface. Our observation of the surface-induced orbital-selective band reconstruction uncovers a promising method to manipulate the properties of the surface and realize possible orbital-selective control of the electronic structure.

2. Experimental details and results

Single crystals of CsV_3Sb_5 were grown by the self-flux method.[7,10] The samples were cleaved *in-situ* with a base pressure of better than 8×10^{-11} torr. The photoemission measurements were carried out at our lab-based ARPES system with 21.2 eV photons. The energy resolution was ~ 5 meV for the measurements. The Fermi level was referenced to that of a polycrystalline Au in electrical contact with the samples. DFT calculations were performed without spin–orbit-coupling in VASP v5.4.4 using identical parameters to a recent study.[7]

CsV_3Sb_5 is a new kagome superconductor characterized by a layered crystal structure with $P6/mmm$ (No. 191) space group (Fig. 1(a)). The V atoms form a perfect kagome sub-

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lattice in this material. This kagome net is interwoven with Sb atoms, which form a hexagonal net in the same plane (Figs. 1(b) and 1(c)). This V_3Sb layer is then bounded above and below by Sb honeycomb lattices and Cs hexagonal lattices (Fig. 1(a)). The corresponding three-dimensional (3D) Brillouin zone (BZ) is presented in Fig. 1(d). As shown in Figs. 1(e) and 1(f), the measured Fermi surface map and band structure along Γ–M direction are consistent with theoretical calculations.[7] For simplicity, we label the electron-like band around Γ point as α band, and the hole-like band around M point as β band, hereafter (Fig. 1(f)).

Systematic measurements have been performed as a function of time at a fixed temperature (115 K). We note that the measurement temperature is much higher than the transition temperature of any electronic order in this system. By tracking the energy position of the band bottom (top) via the EDC peak at Γ (M) (Fig. 2), the systematic time evolution of the α (β) band is shown in Fig. 2(c) (Fig. 2(f)). It is clear that the α band moves significantly towards a lower binding energy, while the β band shows a moderate energy change as a function of time, giving rise to an apparent momentum-dependent band evolution with time.

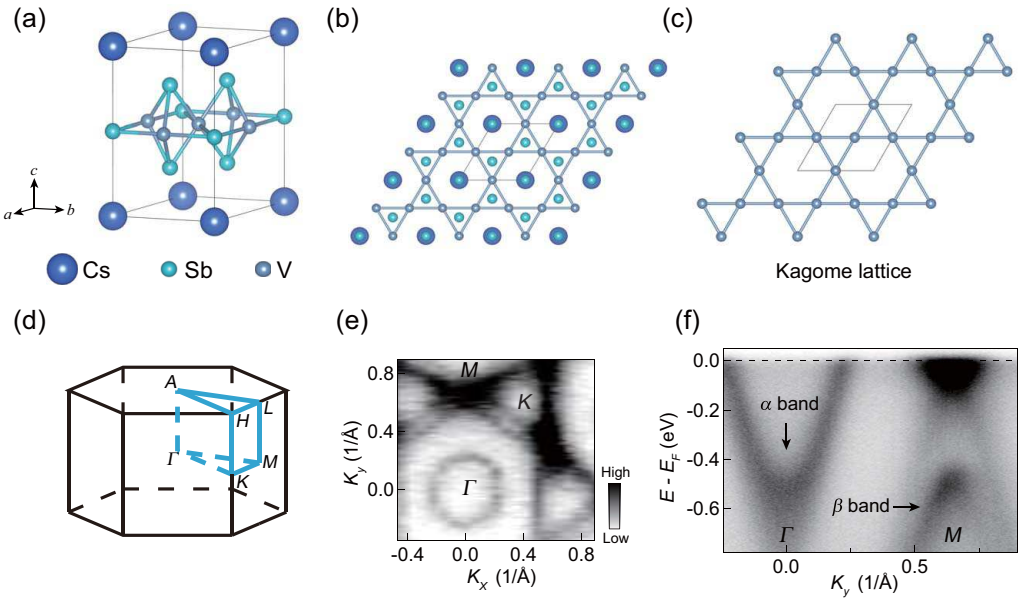


Fig. 1. Crystal structure and band structure of CsV_3Sb_5. (a) The 3D lattice structure of CsV_3Sb_5 with space group $P6/mmm$. (b) Top view of the crystal structure. (c) The kagome sublattice formed by V atoms. (d) Schematic of the 3D BZ. (e) Fermi surface measured at 200 K. (f) Band structure along Γ–M direction measured at 120 K. The measurements were performed on fresh sample surfaces.

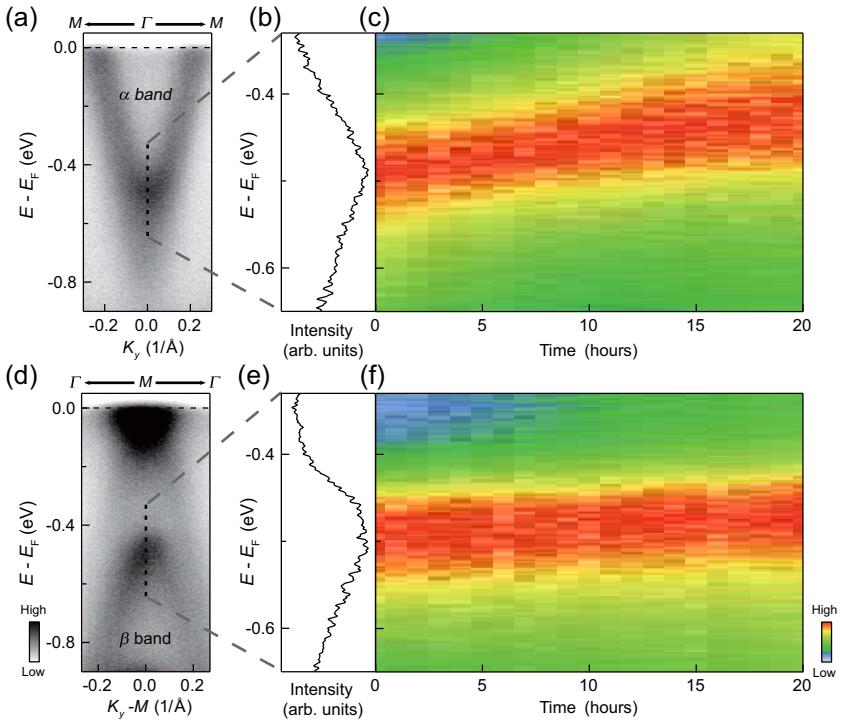


Fig. 2. The evolution of band structure as a function of time. (a) Photoelectron intensity plot of the α band near Γ. (b) EDC at Γ with its energy range marked by the black dashed line in (a). (c) Time evolution of the EDC in (b). The intensity of the EDC peak is shown by the color scale. (d)–(f) Same as (a)–(c), but for the β band near M.

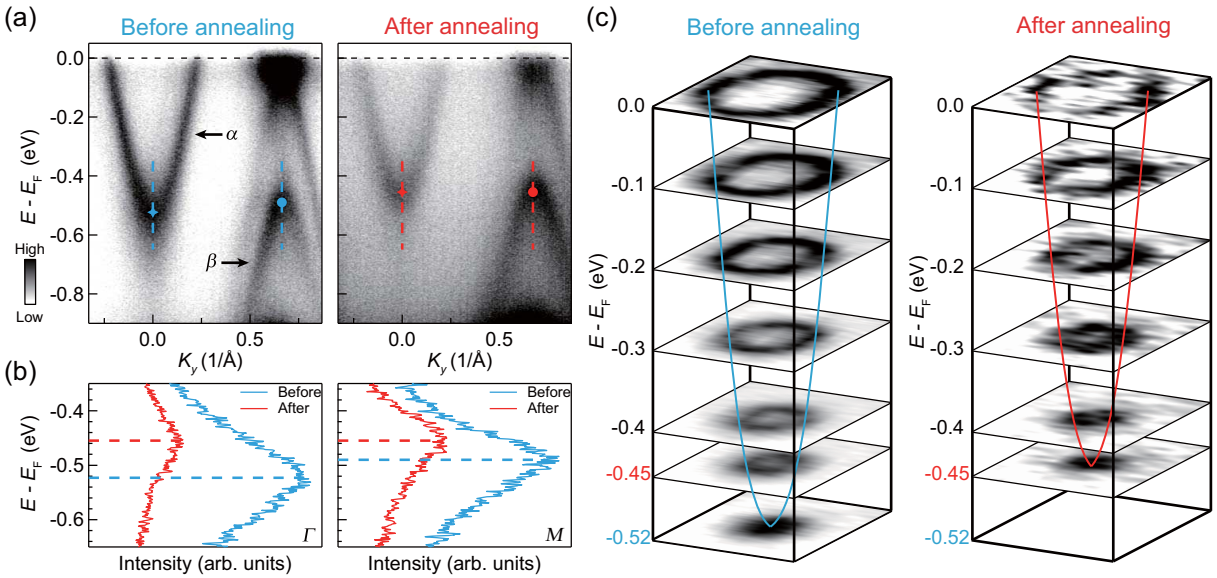


Fig. 3. Momentum-dependent energy shift of the bands with *in-situ* vacuum annealing. (a) Band structure before and after annealing along the Γ–M direction measured at 200 K. (b) EDCs before (blue) and after (red) annealing. The corresponding energy range is marked by the dash lines in (a). (c) Constant energy maps around Γ point before and after annealing. Blue and red lines are guides to the eyes.

To better understand the band evolution, we have further performed measurements before and after an *in-situ* vacuum annealing process (Fig. 3). Figure 3(a) shows the band structure along Γ–M direction measured before and after a two-hour-annealing at 200 °C respectively. These two measurements have been carried out with the same condition and at the same temperature (200 K). By comparing the energy position of α (β) band bottom (top) via the EDC peak before and after the annealing process, a momentum-dependent energy shift of the bands is observed, mimicking that observed in the previous time-dependent experiment. We note that the same amount of energy shift is now realized in a much shorter time scale with the annealing process (Fig. 3(b)). The significant energy shift of the α band can also be resolved from the constant energy map at various binding energies. As the binding energy becomes larger, the constant energy contour gradually shrinks from a circular shape to a point. The location of this vanishing point is at a smaller binding energy in the measurement after annealing, comparing to that before the annealing process (Fig. 3(c)). The vacuum annealing not only reproduces the momentum-dependent energy shift of the bands, but also accelerates this band evolution.

3. Discussion

We next consider the origins of the time- and momentum-dependent band reconstruction. First, a time-dependent band evolution is presumably associated with changes on the sample surface.[15,33] This is confirmed by the experimental fact that the original band structure (without any energy shift of the bands) appears again when a fresh surface is produced by re-cleaving the measured samples. However, the observed momentum-dependent band evolution is not due to a trivial aging effect. Sample aging would typically broaden the measured spectrum but should not give rise to an energy shift of the bands. Carrier doping due to a potential absorption of atoms or molecules on the sample surface may induce a rigid band shift, but it cannot explain the different evolution between α band and β band observed in our experiment. To deepen the understanding of the momentum-dependent band evolution, orbital-resolved DFT calculations have been carried out. The calculated band structure (Fig. 4(a)) matches well with our experiment results. As shown in Figs. 4(c) and 4(d), the α band is dominated by Sb p_z-orbital, whereas the β band mainly contains V d-orbital. The p_z-orbital is presumably more sensitive to the out-of-plane interaction. As such, the α band shows a more evident response to the surface changes, which is consistent with our experiment results. Combining the experiments and theoretical calculations, a surface-induced orbital-selective band reconstruction is presented in this compound.

The last thing to discuss is the origin of the sample surface change. We attribute it to the formation of Cs vacancies on the surface. First, due to the chemical activity of Cs atoms and the weak interlayer interaction, the Cs atoms can slowly desorb from the topmost layers of the cleaved surface, producing Cs vacancies on the surface. The formation of alkali-metal-atom vacancies on the cleaved sample surface has been observed by STM measurements.[33] Theoretically, the carriers from the Cs atoms hybridize with both Sb p_z-orbital electrons and V d-orbital electrons, but the hybridization strength is different. In the calculations, the appearance of Cs vacancies induces a significant energy shift of the α band and a moderate energy shift of the β band.[15,34] The same calculations[15] also reveal significant changes of the bands near E_F around the M point, which are also consistent with the experimental

observations in Fig. 3(a)). If the above scenario is at work, and the number of desorbed Cs atoms on the sample surface is increasing with time, then the observed time- and momentum-dependent energy shift of the bands can be well explained. This is also aligned with the fact that high temperature annealing can accelerate the desorption process of Cs atoms on the sample surface, which in turn produces the same momentum-dependent band evolution in a much shorter time. Nevertheless, the high temperature annealing process might be more complicated, since the Cs vacancies may also exist in the bulk sample, at least in a few layers below the surface. In this sense, a direct hole doping effect may appear on top of the surface-induced orbital-selective band reconstruction. It would also be interesting to explore how the physical properties are affected by the Cs vacancies in the material. It has been reported that the loss of Cs atoms in CsV_3Sb_5 thin films can enhance the superconducting transition temperature and suppress the charge density wave.[15]

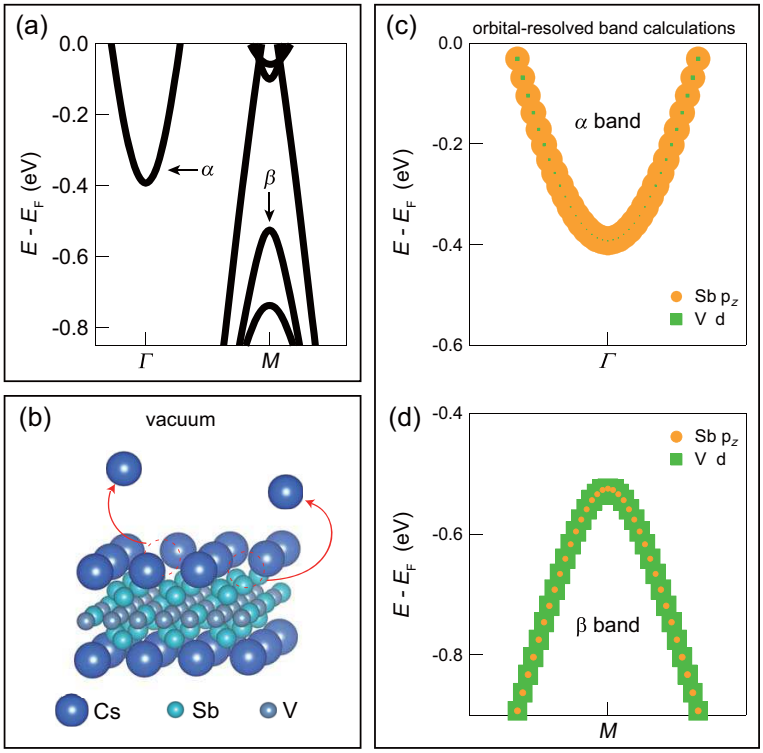


Fig. 4. Orbital-resolved DFT band structure and schematic diagram of the Cs desorption on the sample surface. (a) Calculated band structure along the Γ–M direction. (b) Schematic diagram of the Cs desorption on the sample surface. (c) and (d) Orbital-resolved calculations for α band and β band, respectively.

4. Conclusions

In summary, utilizing high-resolution ARPES measurements, we have identified a surface induced orbital-selective energy shift of the bands in CsV_3Sb_5. A momentum-dependent band evolution is observed as a function of time in the normal state of CsV_3Sb_5. This process is reproduced in a much shorter time scale by annealing the sample in vacuum. Combining the experimental results with orbital-resolved DFT calculations, we illustrate that the observed band evolution represents an orbital-selective energy shift of the bands, which is likely due to the desorption of Cs atoms on the sample surface. These results may pave a special way to manipulate the electronic structure of kagome superconductors via the sample surface. Further studies are stimulated to explore various ways beyond the vacuum annealing to modify the surface of kagome superconductors.

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References

[1] Guo H M and Franz M T 2009 *Phys. Rev. B* **80** 113102
[2] Kang M, Fang S, Ye L, Po H C, Denlinger J, Jozwiak C, Bostwick A, Rotenberg E, Kaxiras E, Checkelsky J G and Comin R 2020 *Nat. Commun.* **11** 4004
[3] Hermele M, Ran Y, Lee P A and Wen X G 2008 *Phys. Rev. B* **77** 224413
[4] Han T H, Helton J S, Chu S, Nocera D G, Rodriguez-Rivera J A, Broholm C and Lee Y S 2012 *Nature* **492** 406
[5] Yu S L and Li J X 2012 *Phys. Rev. B* **85** 144402
[6] Mielke III C, Qin Y, Yin J X, Nakamura H, Das D, Guo K, Khasanov R, Chang J, Wang Z Q, Jia S, Nakatsuji S, Amato A, Luetkens H, Xu G, Hasan M Z and Guguchia Z 2021 *Phys. Rev. Mater.* **5** 034803
[7] Ortiz B R, Teicher S M L, Hu Y, Zuo J L, Sarte P M, Schueller E C, Abeykoon A M M, Krogstad M J, Rosenkranz S, Osborn R, Seshadri R, Balents L, He J and Wilson S D 2020 *Phys. Rev. Lett.* **125** 247002
[8] Ortiz B R, Sarte P M, Kenney E M, Graf M J, Teicher S M L, Seshadri R and Wilson S D 2021 *Phys. Rev. Mater.* **5** 034801
[9] Yin Q, Tu Z, Gong C, Fu Y, Yan S and Lei H 2021 *Chin. Phys. Lett.* **38** 037403
[10] Ortiz B R, Gomes L C, Morey J R, Winiarski M, Bordelon M, Mangum J S, Oswald I W H, Rodriguez-Rivera J A, Neilson J R, Wilson S D, Ertekin E, McQueen T M and Toberer E S 2019 *Phys. Rev. Mater.* **3** 094407
[11] Yu F H, Ma D H, Zhuo W Z, Liu S Q, Wen X K, Lei B, Ying J J and Chen X H 2021 *Nat. Commun.* **12** 3645
[12] Ni S, Ma S, Zhang Y, Yuan J, Yang H, Lu Z, Wang N, Sun J, Zhao Z, Li D, Liu S, Zhang H, Chen H, Jin K, Cheng J, Yu L, Zhou F, Dong X, Hu J, Gao H J and Zhao Z 2021 *Chin. Phys. Lett.* **38** 057403
[13] Chen K Y, Wang N N, Yin Q W, Gu Y H, Jiang K, Tu Z J, Gong C S, Uwatoko Y, Sun J P, Lei H C, Hu J P and Cheng J G 2021 *Phys. Rev. Lett.* **126** 247001
[14] Duan W, Nie Z, Luo S, Yu F, Ortiz B R, Yin L, Su H, Du F, Wang A, Chen Y, Lu X, Ying J, Wilson S D, Chen X, Song Y and Yuan H 2021 *Sci. China Phys. Mech. Astron.* **64** 107462
[15] Song Y, Ying T, Chen X, Han X, Wu X, Schnyder A P, Huang Y, Guo J and Chen X 2021 *Phys. Rev. Lett.* **127** 237001
[16] Zhao H, Li H, Ortiz B R, Teicher S M L, Park T, Ye M, Wang Z, Balents L, Wilson S D and Zeljkovic I 2021 *Nature* **599** 216
[17] Li H X, Zhang T T, Yilmaz T, Pai Y Y, Marvinney C E, Said A, Yin Q W, Gong C S, Tu Z J, Vescovo E, Nelson C S, Moore R G, Murakami S, Lei H C, Lee H N, Lawrie B J and Miao H 2021 *Phys. Rev. X* **11** 031050
[18] Liang Z, Hou X, Zhang F, Ma W, Wu P, Zhang Z, Yu F, Ying J J, Jiang K, Shan L, Wang Z and Chen X H 2021 *Phys. Rev. X* **11** 031026
[19] Ortiz B R, Teicher S M L, Kautzsch L, Sarte P M, Ratcliff N, Harter J, Ruff J P C, Seshadri R and Wilson S D 2021 *Phys. Rev. X* **11** 041030
[20] Song D W, Zheng L X, Yu F H, Li J, Nie L P, Shan M, Zhao D, Li S J, Kang B L, Wu Z M, Zhou Y B, Sun K L, Liu K, Luo X G, Wang Z Y, Ying J J, Wan X G, Wu T and Chen X H 2022 *Sci. China Phys. Mech. Astron.* **65** 247462
[21] Chen H, Yang H, Hu B, Zhao Z, Yuan J, Xing Y, Qian G, Huang Z, Geng L, Ye Y, Ma S, Ni S, Zhang H, Yin Q, Gong C, Tu Z, Lei H, Tan H, Zhou S, Shen C, Dong X, Yan B, Wang Z and Gao H J 2021 *Nature* **599** 222
[22] Fu Y, Zhao N, Chen Z, Yin Q, Tu Z, Gong C, Xi C, Zhu X, Sun Y, Liu K and Lei H 2021 *Phys. Rev. Lett.* **127** 207002
[23] Hu Y, Teicher S M L, Ortiz B R, Luo Y, Peng S, Huai L, Ma J Z, Plub N C, Wilson S D, He J F and Shi M 2022 *Science Bulletin* **67** 495
[24] Cai Y, Wang Y, Hao Z, Liu Y, Ma X M, Shen Z, Jiang Z, Yang Y, Liu W, Jiang Q, Liu Z, Ye M, Shen D, Sun Z, Chen J, Wang L, Liu C, Lin J, Wang J, Huang B, Mei J W and Chen C 2021 arXiv:2109.12778 [cond-mat.str-el]
[25] Hu Y, Wu X, Ortiz B R, Ju S, Han X, Ma J Z, Plumb N C, Radovic M, Thomale R, Wilson S D, Schnyder A P and Shi M 2021 arXiv:2106.05922 [cond-mat.supr-con]
[26] Luo H, Gao Q, Liu H, Gu Y, Wu D, Yi C, Jia J, Wu S, Luo X, Xu Y, Zhao L, Wang Q, Mao H, Liu G, Zhu Z, Shi Y, Jiang K, Hu J, Xu Z and Zhou X J 2022 *Nat. Commun.* **13** 273
[27] Kang M, Fang S, Kim J K, Ortiz B R, Ryu S H, Kim J, Yoo J, Sangiovanni G, Sante D D, Park B G, Jozwiak C, Bostwick A, Rotenberg E, Kaxiras E, Wilson S D, Park J H and Comin R 2022 *Nat. Phys.* **18** 301
[28] Wang Z, Ma S, Zhang Y, Yang H, Zhao Z, Ou Y, Zhu Y, Ni S, Lu Z, Chen H, Jiang K, Yu L, Zhang Y, Dong X, Hu J, Gao H J and Zhao Z 2021 arXiv:2104.05556 [cond-mat.supr-con]
[29] Liu Z, Zhao N, Yin Q, Gong C, Tu Z, Li M, Song W, Liu Z, Shen D, Huang Y, Liu K, Lei H and Wang S 2021 *Phys. Rev. X* **11** 041010
[30] Cho S, Ma H, Xia W, Yang Y, Liu Z, Huang Z, Jiang Z, Lu X, Liu J, Liu Z, Li J, Wang J, Liu Y, Jia J, Guo Y, Liu J and Shen D 2021 *Phys. Rev. Lett.* **127** 236401
[31] Lou R, Fedorov A, Yin Q, Kuibarov A, Tu Z, Gong C, Schwier E F, Büchner B, Lei H and Borisenko S 2022 *Phys. Rev. Lett.* **128** 036402
[32] Hao Z, Cai Y, Liu Y, Wang Y, Sui X, Ma X M, Shen Z, Jiang Z, Yang Y, Liu W, Jiang Q, Liu Z, Ye M, Shen D, Liu Y, Cui S, Chen J, Wang L, Liu C, Lin J, Wang J, Huang B, Mei J W and Chen C 2021 arXiv:2111.02639 [cond-mat.str-el]
[33] Yu J, Xu Z, Xiao K, Yuan Y, Yin Q, Hu Z, Gong C, Guo Y, Tu Z, Tang P, Lei H, Xue Q K and Li W 2022 *Nano Lett.* **22** 918
[34] LaBollita H and Botana A S 2021 *Phys. Rev. B* **104** 205129