swiss physical society

Nr. 68, Oktober 2022

SPG Mitteilungen
Communications de la SSP

Auszug - Extrait

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The kagome lattice, named after a pattern of Japanese basketry, is a well-known theoretical playground for studying the interplay between frustrated geometry, correlations, and topology. In a recently discovered family of materials, these features combine with superconductivity and an unusual charge order to produce an even richer and more intriguing combination of physical phenomena. The compounds KV_3Sb_5, CsV_3Sb_5, and RbV_3Sb_5 fill a long-standing gap in the available scope of quantum materials and open several avenues for future research.

I. Introduction

The kagome pattern is inspired by a pattern of Japanese basketry and formed by corner-sharing triangles (see Fig. 1a). The crystal lattice derived from this pattern (see Fig. 1b) has been a popular playground in condensed matter physics for more than seventy years. The unique geometry gives rise to frustration, correlated quantum orders, and topology, owing to its special features: the electronic structure shows a flat band, inflection points called 'van Hove singularities', and Dirac cones (see Fig. 1c and d).

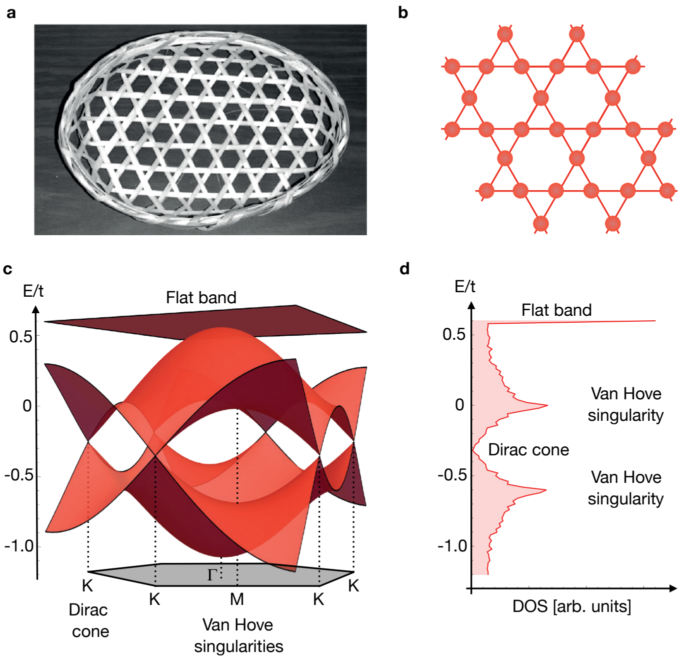

Fig. 1: Kagome systems and their electronic structure. ***a.*** *The kagome pattern originates from Japanese basketry (taken from [1]).* ***b.*** *The kagome lattice consists of corner-sharing triangles.* ***c.*** *The electronic structure contains van Hove singularities, Dirac cones, and a flat band.* ***d.*** *Flat band and van Hove singularities drastically enhance the density of states (DOS), thereby promoting interactions.*

The flat band results from the destructive quantum interference of states localized on the three sublattices, promoting interactions and possibly fractional states. Similarly, van Hove singularities can give rise to correlated orders, too: in graphene, for instance, doping to a van Hove singularity would allow for chiral d-wave superconductivity [2]. In the case of the kagome system, such orders can be enriched by the geometrical frustration of the underlying lattice. Additionally, the Dirac cones give rise to non-trivial topology once spin-orbit coupling is considered, which opens a small gap. However, a material realizing the kagome interplay between frustrated geometry, correlations, and topology has been long awaited. The discovery of the family of kagome metals KV_3Sb_5, CsV_3Sb_5, and RbV_3Sb_5 — commonly abbreviated to AV_3Sb_5 — recently brought this search to a successful end: Realizing motives from the iconic kagome band structure, they exhibit the sought after interaction phenomena by a high-temperature charge order as well as a superconducting instability at lower temperatures [3-7].

II. New kagome materials KV_3Sb_5, CsV_3Sb_5, and RbV_3Sb_5

The compounds KV_3Sb_5, CsV_3Sb_5, and RbV_3Sb_5 are formed by a structurally perfect two-dimensional kagome net of vanadium atoms, which is interwoven with a hexagonal antimony lattice (see Fig. 2a) [3]. Surrounding this core are additional antimony honeycomb layers, furthermore encapsulated by the triangular lattice of either K, Cs, or Rb. The three-membered family, therefore, crystallizes in the hexagonal P 6/mmm space group.

Interestingly, the layered structure gives rise to a quasi-two-dimensional electronic structure, as highlighted for instance by density functional theory results (see Fig. 2b). The band structure is metallic, with just a few bands crossing the Fermi level. These bands form three distinct features, changing only slightly as a function of k_z: (i) a quasi-two-dimensional electron pocket around the Γ point (i.e. the center of the Brillouin zone), (ii) several van Hove singularities at the M point, and (iii) Dirac bands at the K point. Consequently, except for a flat band (which is situated far from the Fermi level and only partially flat), all features of the two-dimensional kagome lattice are present, with a mul-

Glossary

Dirac cone – Feature in the electronic band structure with linear dispersion, where valence and conduction band are conically shaped. Dirac cones act as sources and sinks of Berry curvature, being essential for topological phases.

Van Hove singularity – Point in the electronic band structure with vanishing group velocity and singular density of states.

Charge order – Phase in strongly correlated materials, where interactions lead to a reordering of charges. The charge order transition is usually accompanied by symmetry breaking, for instance if charges reorder in a superlattice, breaking the original translational symmetry of the underlying crystal.

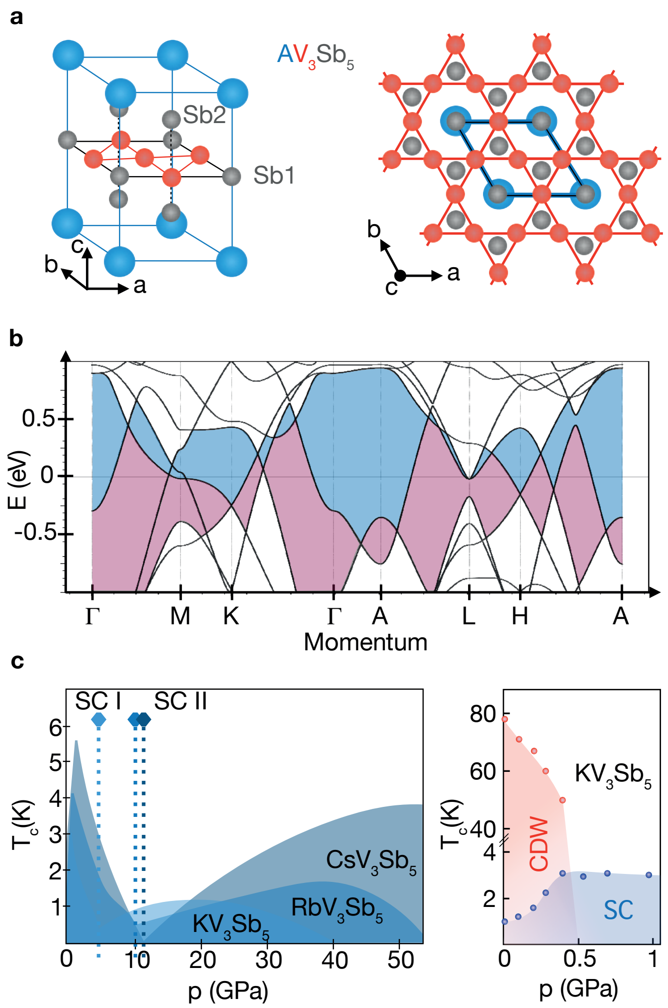

*Fig. 2: Exotic quantum phases in the kagome materials AV_3Sb_5. **a.** AV_3Sb_5 forms a layered structure in the P6/mmm space group. The vanadium kagome lattice is interwoven with a hexagonal antimony lattice, further encapsulated by an antimony honeycomb sheet. The family of kagome superconductors is formed by outer hexagonal sheets of A = K, Cs, Rb (taken from [33]). **b.** Band structure of KV_3Sb_5 along high symmetry directions in the Brillouin zone. The direct gap (shaded area) carries a non-trivial Z_2 topological index (taken from [33]). **c.** All members of the family show a superconducting phase diagram with two domes. The charge-ordered phase in KV_3Sb_5 enters competition with superconductivity at around 0.5 GPa and is suppressed as pressure increases. Depiction reproduced from [33], following data from [8, 9, 16, 17].*

titude of van Hove singularities at the Fermi level. Importantly, these compounds are non-magnetic, differentiating them from previously known magnetic kagome systems, like for instance Fe_3Sn_2.

The presence of van Hove singularities at the Fermi level promotes interactions, resulting in a set of correlated phases: when cooling below room temperature, all compounds show the onset of a charge order, with slightly varying critical temperatures (T_{CO} = 78 K, 94 K, and 102 K for A = K, Cs, and Rb, respectively [8-10]). When considering even lower temperatures, the charge order coexists with a superconducting phase (T_{SC} = 0.93 K, 2.5 K, and 0.92 K for A = K, Cs, and Rb, respectively [11-13]). When pressure is applied, the charge order is rapidly suppressed and superconductivity is promoted to higher transition temperatures, revealing their competing nature. For higher pressures, a second superconducting dome appears, separated from the first one (see Fig. 2c) [8, 9, 16, 17]. Even though both charge order and superconductivity are robust and have been observed in a wide range of samples and techniques, the exact nature of these phases still remains to be determined.

III. Evidence for chiral charge order

The unique feature of AV_3Sb_5 is the emergence of a *chiral* charge order with both electronic and magnetic anomalies. The charge order is commonly believed to be driven by the van Hove singularities at the Fermi level, opening a strongly momentum-dependent gap [16-18]. Additionally, experiments provide evidence for a chiral charge order: the ordering vectors obtained from scanning tunneling microscopy show anisotropic intensities, defining a chirality (see Fig. 3a) [19-21]. This chirality can be switched by an external magnetic field, indicating the presence of orbital currents [22-24]. Such currents would break time-reversal symmetry, which is supported by Kerr effect measurements [25-28]. Theoretically, these features could be explained by a complex order parameter realizing a higher angular momentum state, dubbed *unconventional*, in analogy to superconducting orders [30].

The unconventional nature of the charge order reflects in special transport signatures: time-reversal symmetry breaking is reflected by a giant anomalous Hall effect and an anomalous Nernst signal (see Fig. 3b) [31]. Moreover, the chiral nature of the charge order could be mirrored in an observed electronic magneto-chiral anisotropy (see Fig. 3c) [32].

While the emergence of a charge order can be regarded as a common phenomenon, the chiral and higher angular momentum nature is truly exceptional [33]. The emergence of all of these features is a hallmark of the kagome platform, combining geometrical frustration, charge order, and topology.

IV. Superconductivity and its interplay with the charge order

Upon lowering the temperature of the material, AV_3Sb_5 is found to also enter a superconducting state. The mechanism of superconductivity is reflected in the symmetry of Cooper pairing, which, on the kagome lattice, holds promise for unconventional phases. The spin and orbital aspects of the superconducting order are, however, still under investigation: experimental evidence exists for both a singlet [34] or a triplet spin structure [35-37], while the band structure was observed to be either fully gapped [11, 34, 40, 41] or having gap nodes [20, 36, 38, 40]. Interestingly, the pairing nature seems to differ between the three compounds: while KV_3Sb_5 and RbV_3Sb_5 show a nodal superconducting gap structure [23], CsV_3Sb_5 displays a two-gap (s+s)-wave symmetry in muon spin relaxation experiments [42]. The complex Fermi surface structure with multiple gaps [20, 36, 38, 40] inspired a multitude of theoretical proposals, including f-wave order parameters (see Fig. 4a) [43], pair density waves [44] and higher charge Cooper pairs [45]. The latter charge-4e and charge-6e superconductivity could explain recent experiments on a so-called “thick-rim geometry”, showing oscillations of the resistance with an unusual periodicity that would be explainable with such exotic pairings [46]. Even though the low-temperature behavior of AV_3Sb_5 is not yet conclusively understood, the presence of a chiral charge or-

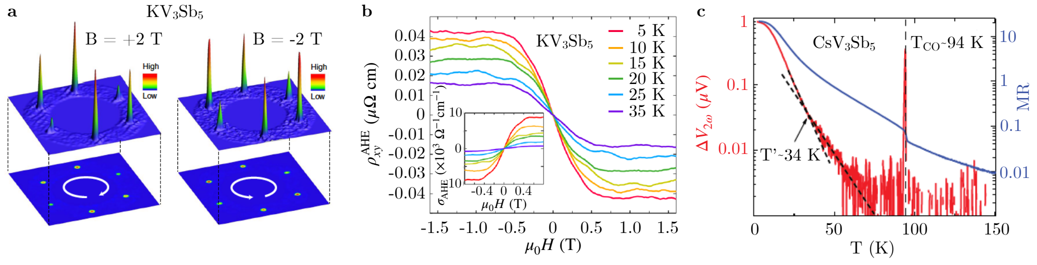

Fig. 3: Chiral charge order in AV$_3$Sb$_5$. ***a.*** *Chirality reversal of the spectroscopic 2x2 vector peaks under an applied magnetic field in KV$_3$Sb$_5$ indicates the chiral nature of the charge order (taken from [19].* ***b.*** *Large anomalous Hall effect (AHE) indicates time reversal symmetry breaking: ρ_{xy}^{AHE} is obtained by subtracting the ordinary Hall background at various temperatures. The inset shows the corresponding conductivity σ_{xy}^{AHE} at various temperatures (taken from [29]).* ***c.*** *Log-scale temperature dependence of $\Delta V_{2\omega}$ and magnetoresistance ratio MR. The transition into the CDW state is evident as a sharp spike in $\Delta V_{2\omega}$, while the significant increase at lower temperature suggests the onset of chiral ordering (taken from [32]).*

der fuels hopes for likewise unconventional features. One piece of evidence in this direction is the critical scaling of the superfluid density with the critical temperature, placing AV$_3$Sb$_5$ close to unconventional superconductors with a low density of Cooper pairs (see Fig. 4e) [22].

However, the presence of two correlated orders — charge order and superconductivity — begs the question of whether they act as accomplices or opponents: while they can result from the same interaction terms, they compete for gapping out the same Fermi surface. The competition of both orders can be manipulated by straining the samples, applying pressure, or carrier doping, showing suppression of the charge order and enhancement of superconductivity (see Fig. 2c and 4 b,c) [8, 9, 16, 47-49]. Surprisingly, once the charge order is suppressed, all three compounds show a nodeless superconducting gap with time-reversal symmetry breaking (see Fig. 4d) [23, 50].

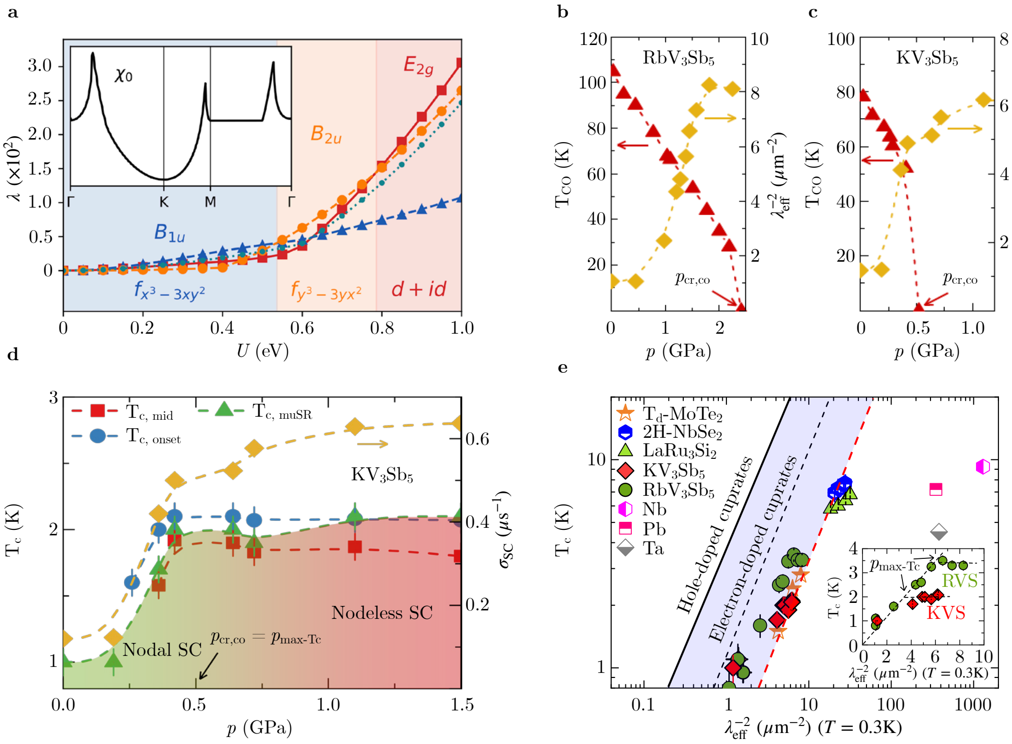

Fig. 4: Superconductivity in AV$_3$Sb$_5$. ***a.*** *Theoretical proposal for the superconducting order parameter. Pairing strength eigenvalues λ for the dominant superconducting instabilities are displayed as a function of the on-site Coulomb interaction U. Continuous (dashed) lines indicate triplet (singlet) pairing. Two distinct f-wave solutions dominate for smaller interaction scales until a d-wave solution dominates for larger U. The upper left inset depicts the largest eigenvalue trajectory of the bare susceptibility χ_0 along the high-symmetry path (taken from [43]).* ***b.*** *and* ***c.*** *Pressure dependence of the superfluid density and the charge order temperature T_{CO} for RbV$_3$Sb$_5$ and KV$_3$Sb$_5$ (taken from [23]).* ***d.*** *Pressure dependence of the superconducting transition temperature and the base-T value of the superconducting muon spin depolarization rate. Crossover from nodal to nodeless superconducting pairing is denoted by color (taken from [23]).* ***e.*** *Plot of T_c versus the superfluid density in logarithmic scale obtained from muon spin relaxation experiments in KV$_3$Sb$_5$ and RbV$_3$Sb$_5$, with comparison to the kagome superconductor LaRu$_3$Si$_2$ as well as for the layered transition metal dichalcogenide superconductors Td-MoTe$_2$ and 2H-NbSe$_2$ (dashed red line) and various conventional Bardeen-Cooper-Schrieffer superconductors (taken from [23]). Inset shows the plot in a linear scale.*

The multifaceted possibilities to manipulate the orders offer a unique opportunity to study the interplay of superconductivity and charge order, possibly leading to the design of systems with higher critical temperatures.

V. Discussion

The kagome materials AV$_3$Sb$_5$ show an exciting range of physical properties, with several details still under investigation. These observations have to be carefully analyzed with respect to the employed experimental probes: for instance, surface sensitive as compared to bulk specific techniques lead to different observations of the translational symmetry breaking in the charge-ordered regime. Moreover, whether the charge order entails an additional transition to a nematic order, is still under discussion. Apart from different experiments, strain in the sample or different chemical compositions can also lead to divergent results. For instance, nodes in the superconducting gap might disappear when the charge order is suppressed by pressure, strain, or doping (see Fig. 4d). Consequently, the character of the superconducting phase is strongly dependent on the competition with the preceding charge order.

VI. Future Perspectives

AV$_3$Sb$_5$ is a valuable resource for building quantum matter by design, opening several avenues for future research. The quasi-two-dimensional structure of AV$_3$Sb$_5$ naturally leads to the question of whether thin layers or even monolayers can be exfoliated. Thin films would allow to form Moire structures by gating, stacking, or twisting, promising exciting future developments. Moreover, the engineering by strain and pressure offers to manipulate the phases in a controlled manner. This could also facilitate the further exploration of the superconducting phase. Additionally, the unique transport signatures provide interesting questions for the future: How is the nonlinear response reflected in the superconducting regime? How can the strong anomalous Hall effect be manipulated or modified? Understanding the response to external fields could pave the way to potential applications.

The family of kagome materials AV_3Sb_5 fills a long-standing gap in the available scope of quantum materials, showing exciting orders emerging from strong correlations. The possibility to engineer and tune these phases holds promise for even more exciting discoveries.

The authors acknowledge all collaborators and involved funding schemes.

References

[1] Mamoru Mekata. Kagome: The Story of the Basketweave Lattice. *Physics Today* **56**, 12-13 (2003).

[2] Nandkishore, R., Levitov, L. & Chubukov, A. Chiral superconductivity from repulsive interactions in doped graphene. *Nature Phys* **8**, 158–163 (2012).

[3] Ortiz, B. R. et al. New kagome prototype materials: discovery of KV_3Sb_5, RbV_3Sb_5, and CsV_3Sb_5. *Phys. Rev. Materials* **3**, 094407 (2019).

[4] Kiesel, M. L. & Thomale, R., Sublattice interference in the kagome Hubbard model. *Phys. Rev.* **B 86**, 121105 (2012).

[5] Yu, S.-L. & Li, J.-X., Chiral superconducting phase and chiral spin-density-wave phase in a Hubbard model on the kagome lattice. *Phys. Rev.* **B 85**, 144402 (2012).

[6] Wang, W.-S., Li, Z.-Z., Xiang, Y.-Y. & Wang, Q.-H., Competing electronic orders on kagome lattices at van Hove filling. *Phys. Rev.* **B 87**, 115135 (2013).

[7] Kiesel, M. L., Platt, C. & Thomale, R., Unconventional Fermi Surface Instabilities in the Kagome Hubbard Model. *Phys. Rev. Lett.* **110**, 126405 (2013).

[8] Du, F. et al., Pressure-induced double superconducting domes and charge instability in the kagome metal KV_3Sb_5. *Phys. Rev.* **B 103**, L220504 (2021).

[9] Chen, K. Y. et al., Double Superconducting Dome and Triple Enhancement of T_c in the Kagome Superconductor CsV_3Sb_5 under High Pressure. *Phys. Rev. Lett.* **126**, 247001 (2021).

[10] Li, H. et al., Observation of Unconventional Charge Density Wave without Acoustic Phonon Anomaly in Kagome Superconductors AV_3Sb_5 (A = Rb, Cs). *Phys. Rev.* **X 11**, 031050 (2021).

[11] Ortiz, B. R. et al., Superconductivity in the Z_2 kagome metal KV_3Sb_5. *Phys. Rev. Materials* **5**, 034801 (2021).

[12] Ortiz, B. R. et al., CsV_3Sb_5: A Z_2 Topological Kagome Metal with a Superconducting Ground State. *Phys. Rev. Lett.* **125**, 247002 (2020).

[13] Yin, Q. et al., Superconductivity and Normal-State Properties of Kagome Metal RbV_3Sb_5 Single Crystals. *Chinese Physics Letters* **38**, 037403 (2021).

[14] Zhao, C. C. et al., Nodal superconductivity and superconducting domes in the topological Kagome metal CsV_3Sb_5. arXiv e-prints (2021).

[15] Zhu, C. C. et al., Double-dome superconductivity under pressure in the V-based Kagome metals AV_3Sb_5 (A = Rb and K). arXiv e-prints (2021).

[16] Luo, H. et al., Electronic Nature of Charge Density Wave and Electron-Phonon Coupling in Kagome Superconductor KV_3Sb_5. *Nature Communications*, 13, 273 (2022)

[17] Wang, Z. et al., Distinctive momentum dependent charge-density-wave gap observed in CsV_3Sb_5 superconductor with topological Kagome lattice. arXiv e-prints (2021).

[18] Nakayama, K. et al., Multiple Energy Scales and Anisotropic Energy Gap in the Charge-Density-Wave Phase of Kagome Superconductor CsV_3Sb_5. *Phys. Rev.* **B 104**, L161112 (2021).

[19] Jiang, Y.-X. et al., Unconventional chiral charge order in kagome superconductor KV_3Sb_5. *Nature Materials* **20**, 1353-1357 (2021), Springer Nature.

[20] Wang, Z. et al., Electronic nature of chiral charge order in the kagome superconductor CsV_3Sb_5. *Phys. Rev.* **B 104**, 075148 (2021).

[21] Shumiya, N. et al., Intrinsic nature of chiral charge order in the kagome superconductor RbV_3Sb_5. *Phys. Rev.* **B 104**, 035131 (2021).

[22] Mielke, C., Guguchia, Z., et al., Time-reversal symmetry-breaking charge order in a correlated kagome superconductor. *Nature* **602**, 245-250 (2022), Springer Nature.

[23] Guguchia, Z. et al., Tunable nodal kagome superconductivity in charge ordered RbV_3Sb_5. arXiv e-prints (2021).

[24] Khasanov, R. et. al., Time-reversal symmetry broken by charge order in CsV_3Sb_5. *Physical Review Research* **4**, 023244 (2022).

[25] Gan, Y. et al., Magneto-Seebeck effect and ambipolar Nernst effect in the CsV_3Sb_5 superconductor. *Phys. Rev.* **B** 104, L180508 (2021).

[26] Chen, D. et al., Anomalous thermoelectric effects and quantum oscillations in the kagome metal CsV_3Sb_5. *Phys. Rev.* **B 105**, L201109 (2022).

[27] Xu, Y. et al., Universal three-state nematicity and magneto-optical Kerr effect in the charge density waves in AV_3Sb_5 (A = Cs, Rb, K). arXiv e-prints (2022).

[28] Hu, Y. et. al., Time-reversal symmetry breaking in charge density wave of CsV_3Sb_5 detected by polar Kerr effect. arXiv e-prints (2022).

[29] Yang, S.-Y. et. al., Giant, unconventional anomalous Hall effect in the metallic frustrated magnet candidate, KV_3Sb_5. *Sci. Adv.* **6**, 1-7s (2020).

[30] Denner, M. M., Thomale, R. & Neupert, T., Analysis of charge order in the kagome metal AV_3Sb_5 (A = K, Rb, Cs). *Phys. Rev. Lett.* **127**, 217601 (2021).

[31] Zhou, X. et al., Anomalous thermal Hall effect and anomalous Nernst effect of CsV_3Sb_5. arXiv e-prints (2022).

[32] Guo, C. et al., Field-tuned chiral transport in charge-ordered CsV_3Sb_5. arXiv e-prints (2021).

[33] Neupert, T. et al., Charge order and superconductivity in kagome materials. *Nature Physics* **18** (2), 137-143 (2021), Springer Nature.

[34] Mu, C. et al., S-wave superconductivity in kagome metal CsV_3Sb_5 revealed by $^{121/123}$Sb NQR and ^{51}V NMR measurements. *Chinese Physics Letters* **38**, 077402 (2021).

[35] Xiang, Y. et al., Nematic electronic state and twofold symmetry of superconductivity in the topological kagome metal CsV_3Sb_5. *Nature Communications* **12**, 6727 (2021).

[36] Wang, Y. et al., Proximity-induced spin-triplet superconductivity and edge supercurrent in the topological Kagome metal, $K_{1-x}V_3Sb_5$. arXiv e-prints (2020).

[37] Ni, S. et al., Anisotropic superconducting properties of kagome metal CsV_3Sb_5. *Chinese Physics Letters* **38**, 057403 (2021).

[38] Liang, Z. et al., Three-Dimensional Charge Density Wave and Surface-Dependent Vortex-Core States in a Kagome Superconductor CsV_3Sb_5. *Phys. Rev.* **X 11**, 031026 (2021).

[39] Chen, H. et al., Roton pair density wave and unconventional strong-coupling superconductivity in a topological kagome metal. *Nature* **559**, 222 (2021).

[40] Xu, H.-S. et al., Multiband superconductivity with sign-preserving order parameter in kagome superconductor CsV_3Sb_5. *Phys. Rev. Lett.* **127**, 187004 (2021).

[41] Duan, W. et al., Nodeless superconductivity in the kagome metal CsV_3Sb_5. *Science China Physics, Mechanics & Astronomy* **64**, 107462 (2021).

[42] Gupta, R. et al., Microscopic evidence for anisotropic multigap superconductivity in the CsV_3Sb_5 kagome superconductor. *npj Quantum Mater.* **7**, 49 (2022).

[43] Wu, X. et al., Nature of unconventional pairing in the kagome superconductors AV_3Sb_5. *Phys. Rev. Lett.* **127** (17), 177001 (2021).

[44] Zhou, S. et al., Doped orbital Chern insulator, Chern Fermi pockets, and chiral topological pair density wave in kagome superconductors. arXiv e-prints (2022).

[45] Han, J. H. et al., Understanding resistance oscillation in CsV_3Sb_5 superconductor. arXiv e-prints (2022).

[46] Ge, J. et al., Discovery of charge-4e and charge-6e superconductivity in kagome superconductor CsV_3Sb_5. arXiv e-prints (2022).

[47] Yu, F. H. et al., Unusual competition of superconductivity and charge-density-wave state in a compressed topological kagome metal. *Nature Communications* **12**, 3645 (2021).

[48] Qian, T. et al., Revealing the competition between charge density wave and superconductivity in CsV_3Sb_5 through uniaxial strain. *Phys. Rev.* **B 104**, 144506 (2021).

[49] Oey, Y. M. et al., Fermi level tuning and double-dome superconductivity in the kagome metal $CsV_3Sb_{5-x}Sn_x$, *Phys. Rev. Materials* **6**, L041801 (2022).

[50] Gupta, R. et. al., Two types of charge order in the superconducting kagome material CsV_3Sb_5. *Communications Physics*, in press.