Charge density wave in kagome lattice intermetallic ScV₆Sn₆

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Materials hosting kagome lattices have drawn interest for the diverse magnetic and electronic states generated by geometric frustration. In the AV₃Sb₅ compounds (A = K, Rb, Cs), stacked vanadium kagome layers give rise to unusual charge density waves (CDW) and superconductivity. Here we report single-crystal growth and characterization of ScV₆Sn₆, a hexagonal HfFe₆Ge₆-type compound that shares this structural motif. We identify a first-order phase transition at 92 K. Single crystal X-ray and neutron diffraction reveal a charge density wave modulation of the atomic lattice below this temperature. This is a distinctly different structural mode than that observed in the AV₃Sb₅ compounds, but both modes have been anticipated in kagome metals. The diverse HfFe₆Ge₆ family offers more opportunities to tune ScV₆Sn₆ and explore density wave order in kagome lattice materials.

Geometrically frustrated atomic arrangements hold special interest for condensed matter physics. One example, the kagome lattice, is composed of triangles and hexagons (Fig. 1(a)). Tight binding models yield an electronic structure hosting Dirac nodes, van Hove singularities and flat bands (Fig. 1(b)). Depending on band filling and interactions, a wide variety of electronic states can be realized including charge density waves (CDWs), spin density waves, bond order, and superconductivity.

The hexagonal AV₃Sb₅ compounds (A = K, Rb, Cs) are a rich family of strongly correlated materials. Stacked vanadium kagome layers in these materials give rise to CDWs and superconductivity. The origin of the CDW is closely tied to van Hove singularities at the Fermi level. The unusual characteristics of the CDW and its interaction with superconductivity have sparked great interest in kagome lattice derived charge order.

The hexagonal HfFe₆Ge₆-type “166” compounds are a large family of intermetallics related to CoSn [41,42]. Unlike CoSn and AV₃Sb₅, these RM₆X₆ compounds have two kagome sheets per unit cell separated by alternating RX₂ and X₂ layers (Fig. 1(c)). We focus on the RV₆Sn₆ compounds as they host the vanadium kagome lattice so integral to the exciting behavior in AV₃Sb₅ [43-45]. In fact, the rare earth variants even possess similar filling of the vanadium d-orbital bands [22,23,43-44]. Although the band structure and f-orbital magnetism have garnered some interest in RV₆Sn₆ (R = Y, Gd-Tm, and Lu) [43,46,48,51] no vanadium-driven order has been observed to date.

In this Letter we examine the low-temperature behavior of single crystals of the kagome metal ScV₆Sn₆. Physical property measurements reveal a first-order phase transition around 92 K reminiscent of that in the AV₃Sb₅ compounds. X-ray and neutron diffraction reveal a CDW.
below this temperature that is distinctly different than those in AV$_3$Sb$_5$ [25, 26, 28, 31, 34]. The CDW we identify in ScV$_6$Sn$_6$ demonstrates that charge order is a common feature in partly filled d-orbital kagome systems. Compared to the AV$_3$Sb$_5$ compounds, the HfFe$_6$Ge$_6$-type compounds offer improved tuneability making them an ideal platform to explore the curious CDWs in transition metal kagome systems.

**METHODS**

Single crystals were grown from a molten Sn flux using an atomic ratio of Sc:V:Sn = 1:6:60. Dendritic scandium metal (Alfa Aesar 99.9%), vanadium pieces (Alfa Aesar 99.8%), and Sn shot (Alfa Aesar 99.99+%) were loaded into a 2 ml alumina Canfield crucible set [52]. The crucible assembly was sealed in an argon-filled fused silica ampule. Subsequently, the ampule was heated up to 1150 °C over 12 h followed by a 15 h dwell. Crystals were grown during a slow cool to 780 °C at 1 °C/h. Single crystals were extracted from the melt by centrifuging.

The ScV$_6$Sn$_6$ crystals are nicely faceted metallic barrel-shaped hexagonal blocks roughly 1-3 mm in size and their HfFe$_6$Ge$_6$-type structure was established by powder x-ray diffraction (supplemental information). Sn and VSn$_3$ were removed from crystals with 10 wt% aqueous HCl. Crystal composition was estimated using Energy Dispersive Spectroscopy (EDS) on a polished surface.

Low-temperature lattice parameters were estimated from Rietveld fits of powder x-ray diffraction (PXRD) patterns obtained using a Oxford Phemix closed-cycle helium cryostat on a PANalytical X’pert Pro diffractometer with a Cu $K\alpha$ source.

Single crystal x-ray diffraction (SCXRD) studies were performed at 280 K and 50 K with a Rigaku XtaLAB PRO diffractometer using Mo $K\alpha$ radiation, a Rigaku HyPix-6000HE detector and an Oxford N-HeliX cryocooler. Rigaku Oxford Diffraction CrysalisPro [53] was used for peak indexing and integration and JANA or Shelx for structural refinement [54].

Single crystal neutron diffraction (SCND) was measured at HB-3A DEMAND [55] at the High Flux Isotope Reactor at Oak Ridge National Laboratory using 1.542 Å neutrons from a bent Si-220 monochromator [56]. A $2 \times 2 \times 1$ mm$^3$ crystal of ScV$_6$Sn$_6$ was placed inside a closed-cycle refrigerator (CCR) and the $\frac{11}{3} \frac{10}{3} \frac{10}{3}$ superlattice peak was measured on warming and cooling. $^{119}$Sn Mößbauer spectra of ScV$_6$Sn$_6$ were measured at numerous temperatures on 28 mg/cm$^2$ powder sample using a Janis SH-850 closed-cycle cryostat and a constant-acceleration Wissel drive. A 0.1 mCi $^{119}$Sn source and a 2 in diameter Ametek Tl@NaI detector were employed with a 25 μm Pd foil between sample and detector.

Electrical resistivity measurements were obtained using four electrodes on a bar-shaped polished crystal with current perpendicular to c-axis. Resistivity was measured with a Keithley 2450 SourceMeter and a 2182 Nanovoltmeter setup controlled by LabView. Temperature control and magnetic field were provided by a Quantum Design Physical Property Measurement System (PPMS) with magnetic field along c.

For magnetization measurements, an acid-etched crystal was mounted in a plastic drinking straw in a Quantum Design MPMS 3 using the Vibrating Sample Magnetometer (VSM) option. The moment was measured between 3 and 300 K in a field of 1 T applied perpendicular to c.

Finally, heat capacity measurements were carried out using the heat capacity option of the PPMS with a 7.95 mg crystal mounted with Apiezon N-grease. Data were collected between 2 and 200 K by applying a series of heat pulses that each raised the sample temperature by about 30% and analyzing the sample temperature vs time during heating and the subsequent cooling [57]. Near the transition temperature, heating and cooling curves were processed separately to observe the thermal hysteresis associated with the transition.

**RESULTS**

Figure 2 presents temperature-dependent measurements of ScV$_6$Sn$_6$ revealing a phase transition around 92 K. Magnetic susceptibility ($\chi_m$) in Fig. 2(a) reveals a weak Pauli paramagnetic response [58, 59] slightly larger than the 0.001-0.002 cm$^3$/mol observed for YV$_6$Sn$_6$ [43, 44]. In contrast to the yttrium compound, ScV$_6$Sn$_6$ has an abrupt 20% drop in the susceptibility on cooling through 92 K.

The transition observed in magnetization is corroborated by electrical resistivity, Fig. 2(b). ScV$_6$Sn$_6$ displays metallic resistivity decreasing from 164 to 28 Ω cm from 300 to 2 K and no bulk superconductivity down to 80 mK. Critically, there is a conspicuous 35% drop in resistivity on cooling through 92 K. The YV$_6$Sn$_6$, GdV$_6$Sn$_6$, and TbV$_6$Sn$_6$ do not have a step like feature and have smaller resistivities across the whole temperature range [43, 46].

Heat capacity provides clear evidence that the features in $\chi_m(T)$ and $\rho(T)$ correspond to a bulk phase transition in ScV$_6$Sn$_6$. Figure 2(c) presents the specific heat capacity, $C_p(T)$. A sharp peak in the heat capacity represents the heat of transformation across a first-order phase transition. This first-order nature of the transition is evident in the discontinuities in $\chi_m(T)$ and $\rho(T)$ as well as the ~ 0.3-1 K thermal hysteresis observed in these measurements.

The temperature dependence of the lattice parameters in Fig. 2(d) demonstrates that the phase transition
in ScV₆Sn₆ couples to the crystal lattice. On cooling through the 92 K transition, c increases by 0.04% but a remains relatively unchanged.

SCXRD reveals a CDW below the 92 K phase transition in ScV₆Sn₆. Figure 3 (a) presents the diffracted intensity in the HHL plane at 280 and 50 K. On cooling, new spots are observed which can be indexed by a \( \frac{1}{3} \frac{1}{3} \frac{1}{3} \) propagation vector. These superlattice peaks are evidence of a commensurate CDW, a periodic displacement of the atom lattice. SCND reveal that superlattice peak intensity appears near 92 K and grows on cooling (Fig. 3(b)) demonstrating the connection between the CDW and the transition evident in Fig. 2.

The refined R32 low temperature structure is presented in supplemental materials and is dominated by the displacement mode transforming as the irreducible representation \( P_1 \) of \( P6/mmm \) (notation from ISODISTORT and Amplimodes applications). Mössbauer spectroscopy reveals that the Sn atoms see this structural modulation \((\mathbf{c})\). On cooling through the 92K transition the absorption spectra abruptly change shape as reflected by a step of the average quadrupole splitting (Fig. 3c and supplemental materials).

**DISCUSSION**

The CDW in ScV₆Sn₆ has similarities to the CDWs in the AV₃Sb₃ compounds. First, both compounds host vanadium kagome lattices with V-V distances between 2.73 and 2.75 Å. The Fermi level sits within vanadium d-orbital bands in both the AV₃Sb₃ compounds and GdV₆Sn₆ [43, 44, 48, 49]. It is likely that the vanadium bands play a key role in CDW formation in ScV₆Sn₆ as they do in the AV₃Sb₃ compounds [25, 27, 29].

Second, the CDWs in these compounds have a similar impact on the physical properties in these materials. For example, the CDW in CsV₃Sb₃ is accompanied by a sharp drop of both magnetic susceptibility and in-plane resistivity on cooling just as we observe in Fig. 2. Discontinuities in resistance and magnetic susceptibility are frequent signatures of CDW modifications of the electronic structure.

Importantly, the CDWs in AV₃Sb₃ family and ScV₆Sn₆ have two important differences. First, the modulation wave vectors in the two compounds are different. We observe a \( \frac{1}{4} \frac{1}{4} \frac{1}{4} \) wave vector in ScV₆Sn₆ tripling the ab-plane area of the cell (Fig. 3(d)). Along c, the rhombohedral structure repeats every three unit cells (Fig. 3(e) and supplemental information). In contrast, the \( \frac{1}{1} \frac{1}{2} \) or \( \frac{1}{1} \frac{1}{2} \) wave vector in the AV₃Sb₃ compounds quadruples the unit cell in the ab-plane (Fig. 3(f) and(g)) and doubles or quadruples the c-axis.

The second key difference between the CDWs in these compounds is the displacements of the vanadium atoms. In CsV₃Sb₃, the vanadium atoms displace in the plane by 0.009-0.085 Å forming either the Star of David or trihedral arrangement (Fig. 3(f) and(g)). In contrast, our refinement suggests that Sc and Sn1 have the largest modulated displacements in ScV₆Sn₆. We estimate Sc and Sn1 displace up to 0.16 Å along the c axis. The vanadium atoms appear to have a far weaker response, displacing only 0.004-0.006 Å.

CDWs and bond density waves are prominent instabilities of partly filled kagome bands. Charge order is favored by nearest neighbor Coulomb repulsion for \( \frac{1}{3} \) and \( \frac{1}{3} \) filled kagome bands [5, 9, 12, 19, 21]. In fact, the \( \frac{1}{3} \) and \( \frac{1}{3} \) in-plane modulation of the kagome sheet are favored by nearest neighbor Coulomb repulsion [5, 10, 12]. The weak vanadium displacements we infer from our ScV₆Sn₆ diffraction data could be due to some of the exotic orders.
FIG. 3. Details of the CDW in ScV₆Sn₆ (a) single crystal diffraction intensity in the HHL plane. New peaks at 50K signal a structural modulation with wave-vector $\frac{1}{3} \frac{1}{3} \frac{1}{3}$. (b) Single crystal neutron diffraction intensity from the $\frac{1}{3} \frac{1}{3} \frac{1}{3}$ peak. (c) Average quadrupole splitting for a three site fit to $^{119}$Sn Mössbauer spectra. (d) Kagome lattice with ScV₆Sn₆ unit cell (dark yellow). (e) exaggerated $P_{\frac{1}{3} \frac{1}{3} \frac{1}{3}}$ CDW mode showing 3-times larger in-plane unit cell (light yellow). Shorter and longer bonds are darker and lighter, respectively. (f) Depiction of refined atomic displacements in $\frac{1}{3} \frac{1}{3} \frac{1}{3}$ CDW mode in a (1 -1 0) plane of ScV₆Sn₆. (g) and (h) The star of David and tri-hexagonal CDW modulations of the vanadium kagome lattice in CsV₃Sb₅. These $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ or $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ modes quadruple the unit cell in the ab-plane (light yellow rhombi).

proposed in the kagome lattice involving chiral currents and bond orders [7] [12] [13] [16] [17] [21] [30] [34].

Upcoming investigations of the CDW in ScV₆Sn₆ have a distinct advantage over the AV₃Sb₅ compounds: tunability. Although KV₃Sb₅, RbV₃Sb₅, CsV₃Sb₅ compounds have generated significant excitement, the family is quite small [22] (despite proposed variants [70]). Doping opportunities are also limited to Ti or Nb for V [71] [72] and Sn for Sb [39] [23]. In contrast, the RM₆X₆ compounds of the HfFe₆Ge₆ family are far more diverse [11] offering many different options for tuning the CDW in ScV₆Sn₆ to uncover what factors influence charge order and superconductivity in kagome metals.

CONCLUSION

The intriguing charge density waves (CDWs) in the AV₃Sb₅ compounds inspired us to investigate ScV₆Sn₆. Low-temperature physical property measurements reveal a first-order 92K transition. X-ray and neutron diffraction reveal a CDW modulation of the atomic lattice below this temperature. Despite the similarities between ScV₆Sn₆ and the AV₃Sb₅ compounds, their CDWs have different propagation vectors. Excitingly, ScV₆Sn₆ belongs to a large family of compounds offering more tuning opportunities to explore the origin of charge order in kagome lattice compounds.

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[1] W. Beuling, J. C. Everts, and C. M. Smith, Physical Review B 86, 195129 (2012).
[2] K. Momma and F. Izumi, Journal of Applied Crystallography 44, 1272 (2011).
[3] H.-M. Guo and M. Franz, Physical Review B 80, 113102 (2009).
[4] M. H. Christensen, T. Birol, B. M. Andersen, and R. M. Fernandes, Physical Review B 104, 214513 (2021)
[5] W.-S. Wang, Z.-Z. Li, Y.-Y. Xiang, and Q.-H. Wang, Physical Review B 87, 115135 (2013).
[6] H. Tan, Y. Liu, Z. Wang, and B. Yan, Physical Review Letters 127, 046401 (2021).
[7] X. Feng, K. Jiang, Z. Wang, and J. Hu, Science Bulletin 66, 1384 (2021).
[8] S. V. Isakov, S. Wessel, R. G. Melko, K. Sengupta, and J. Wen, Physical Review Letters 97, 147202 (2006).
[9] A. O’Brien, F. Polinmam, and P. Fulde, Physical Review B 81, 235115 (2010).
[10] A. Ruegg and G. A. Fiete, Physical Review B 83, 165118 (2011).
[11] J. Wen, A. Ruegg, C.-C. J. Wang, and G. A. Fiete, Physical Review B.
[12] S. Nishimoto, M. Nakamura, A. O’Brien, and P. Fulde, Physical Review Letters.
[13] M. L. Kiesel, C. Platt, and R. Thomale, Physical Review Letters.
[14] K. Barros, J. W. F. Venderbos, G.-W. Chern, and C. D. Batista, Physical Review B.
[15] S.-L. Yu and J.-X. Li, Physical Review B 85, 144402 (2012).
[16] M. M. Denner, R. Thomale, and T. Neupert, Physical Review Letters 127, 217601 (2021).
[17] X. Feng, Y. Zhang, K. Jiang, and J. Hu, Physical Review B 104, 165136 (2021).
[18] M. L. Kiesel and R. Thomale, Physical Review B 86, 121105(R) (2012).
[19] F. Ferrari, F. Becca, and R. Valentí, (2022), arXiv:2204.10328 [cond-mat.str-el].
[20] W.-H. Ko, P. A. Lee, and X.-G. Wen, Physical Review B 79, 214502 (2009).
[21] T. Park, M. Ye, and L. Balents, Physical Review B 104, 035142 (2021).
[22] B. R. Ortiz, L. C. Gomes, J. R. Morey, M. Winiarski, M. Bordelon, J. S. Mangum, I. W. H. Oswald, J. A. Rodriguez-Rivera, J. R. Neilson, S. D. Wilson, E. Ertekin, T. M. McQueen, and E. S. Toberer, Physical Review Materials 3, 094407 (2019).
[23] B. R. Ortiz, P. M. Sarte, E. M. Kenney, M. J. Graf, S. M. L. Teicher, R. Seshadri, and S. D. Wilson, Physical Review Materials 5, 034801 (2021).
[24] Q. Yin, Z. Tu, C. Gong, Y. Fu, S. Yan, and H. Lei, Chinese Physics Letters 38, 037403 (2021).
[25] B. R. Ortiz, S. M. L. Teicher, Y. Hu, J. L. Zuo, P. M. Sarte, E. C. Schueller, A. M. M. Abeykoon, M. J. Krogo, G. S. Rosenkranz, R. Osborn, R. Seshadri, L. Ballents, J. He, and S. D. Wilson, Physical Review Letters 125, 247002 (2020).
[26] Z. Liang, X. Hou, F. Zhang, W. Ma, P. Wu, Z. Zhang, F. Yu, J.-J. Ying, K. Jiang, L. Shan, Z. Wang, and X.-H. Chen, Physical Review X 11, 031026 (2021).
[27] M. Kang, S. Pang, J.-K. Kim, B. R. Ortiz, S. H. Ryu, J. Kim, J. Yoo, G. Sangiovanii, D. D. Sante, B.-G. Park, C. Jozwiak, A. Bostwick, E. Rotenberg, E. Kaxiras, S. D. Wilson, J.-H. Park, and R. Comin, Nature Physics 18, 301 (2022).
[28] B. R. Ortiz, S. M. L. Teicher, L. Kautzsch, P. M. Sarte, N. Ratcliff, J. Harter, J. P. C. Ruoff, R. Seshadri, and S. D. Wilson, Physical Review X 11, 041030 (2021).
[29] Y. Hu, X. Wu, B. R. Ortiz, S. Ju, X. Han, J. Ma, N. C. Plumb, M. Radovic, R. Thomale, S. D. Wilson, A. P. Schnyder, and M. Shi, Nature Communications 13, 10.1038/s41467-021-26927-w (2022).
[30] L. Nie, K. Sun, W. Ma, D. Song, L. Zheng, Z. Liang, P. Wu, F. Yu, J. Li, M. Shan, D. Zhao, S. Li, B. Kang, Z. Wu, Y. Zhou, K. Liu, Z. Xiang, J. Ying, Z. Wang, T. Wu, and X. Chen, Nature 604, 59 (2022).
[31] Z. Wang, Y.-X. Jiang, J.-X. Yin, Y. Li, G.-Y. Wang, H.-L. Huang, S. Shao, J. Liu, P. Zhu, N. Shumiya, M. S. Hossain, H. Liu, Y. Shi, J. Duan, X. Li, G. Chang, P. Dai, Z. Ye, G. Xu, Y. Wang, H. Zheng, J. Jia, M. Z. Hasan, and Y. Yao, Physical Review B 104, 075148 (2021).
[32] H. Li, T. T. Zhang, T. Yilmaz, Y. Y. Pai, C. E. Marvinney, A. Said, Q. W. Yin, C. S. Gong, Z. J. Tu, E. Vescovo, C. S. Nelson, R. G. Moore, S. Murakami, H. C. Lei, H. N. Lee, B. J. Lawrie, and H. Miao, Physical Review X 11, 031050 (2021).
[33] F. H. Yu, T. Wu, Z. Y. Wang, B. Lei, W. Z. Zhuo, J. J. Ying, and X. H. Chen, Physical Review B 104, L041103 (2021).
[34] Y.-X. Jiang, J.-X. Yin, M. M. Denner, N. Shumiya, B. R. Ortiz, G. Xu, Z. Guguchia, J. He, M. S. Hossain, X. Liu, J. Ruif, L. Kautzsch, S. S. Zhang, G. Chang, I. Belopoliski, Q. Zhang, T. A. Cochran, D. Multer, M. Litskevich, Z.-J. Cheng, X. P. Yang, Z. Wang, R. Thomale, T. Neupert, S. D. Wilson, and M. Z. Hasan, Nature Materials 20, 1353 (2021).
[35] S.-Y. Yang, Y. Wang, B. R. Ortiz, D. Liu, J. Gayles, E. Derunova, R. Gonzalez-Hernandez, L. Smejkal, Y. Chen, S. S. P. Parkin, S. D. Wilson, E. S. Toberer, T. McQueen, and M. N. Ali, Science Advances 6, 10.1126/sciadv.abb6003 (2020).
[36] F. H. Yu, D. H. Ma, W. Z. Zhuo, S. Q. Liu, X. K. Wen, B. Lei, J. J. Ying, and X. H. Chen, Nature Communications 12, 10.1038/s41467-021-23928-w (2021).
[37] H. Chen, H. Yang, B. Hu, Z. Zhao, J. Yuan, Y. Xing, G. Qian, Z. Huang, G. Li, Y. Ye, S. Ma, S. Ni, H. Zhang, Q. Yin, C. Gong, Z. Tu, H. Lei, T. Tan, S. Zhou, C. Shen, X. Dong, B. Yan, Z. Wang, and H.-J. Gao, Nature 599, 222 (2021).
