Optical studies of structural phase transition in the vanadium-based kagome metal ScV\textsubscript{6}Sn\textsubscript{6}

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In condensed matter physics, materials with kagome lattice exhibit exotic emergent quantum states, including charge density wave (CDW), superconductivity, and magnetism. Very recently, hexagonal kagome metal ScV\textsubscript{6}Sn\textsubscript{6} was found to undergo fascinating first-order structural phase transition at around 92 K and a 3x3x3 CDW modulation. The bulk electronic band properties are enlightened for comprehending the origin of the structural phase transition. Here, we perform a optical spectroscopy study on the monocrystalline compound across the transition temperature. The structural transition gives rise to the abrupt changes of optical spectra without observing gap development behavior. The optical measurements revealed a sudden reconstruction of the band structure after transition. We emphasize that the phase transition is of the first order and distinctly different from the conventional density-wave type condensation. Our results provide insight into the origin of the structural phase transition in the new kagome metal compound.

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I. INTRODUCTION

The unique kagome lattice is a two-dimensional network of corner-sharing triangles which have gained tremendous interests for studying the latent intriguing interplay of frustrated, correlated and topological nontrivial quantum electronic states\textsuperscript{1,4-6}. Tight-binding models suggest that the electronic structure could host Dirac nodes, van Hove singularities and geometrically driven flat bands in kagome lattice\textsuperscript{7,8}. And the fertile electronic ground states of kagome lattice systems could be superconductivity (SC)\textsuperscript{9}, charge density waves (CDW)\textsuperscript{9-11}, spin density waves\textsuperscript{12} or a quantum spin liquid\textsuperscript{13,14}, etc.

The peculiar characteristics of the CDW and its subtle interaction with superconductivity has been constantly explored in various condensed matter systems up to now. Many of those CDW-bearing materials are superconducting\textsuperscript{15}. As known to us, the origin of conventional CDW is most commonly traced to Fermi surface nesting. The unconventional SC and CDW were found to coexist in the new system of the correlated kagome metals AV\textsubscript{3}Sb\textsubscript{5} (A= K, Rb, Cs) series before\textsuperscript{9}, immediately sparking an intense exploration of the novel physics in these materials\textsuperscript{16-20}. Stacked vanadium kagome layers in these materials are deemed to give rise to CDWs and SC. The CDW formation in AV\textsubscript{3}Sb\textsubscript{5} is closely tied to the electron-phonon coupling and the electronic band saddle point nesting\textsuperscript{21-23}. Recently, new hexagonal vanadium-based kagome metals ScV\textsubscript{6}Sn\textsubscript{6} of large HfFe\textsubscript{2}Ge\textsubscript{2}-type (space group: No.191, P6\textsubscript{3}mmm at 300 K) family was discovered to undergo a first-order phase transition at around 92 K, reminiscent of the popular CsV\textsubscript{3}Sb\textsubscript{5} system\textsuperscript{24}, yet no SC has been observed at low temperatures. X-ray diffraction verified that an extra three-dimensional 3x3x3 periodic CDW lattice modulation forms below this temperature. High-pressure transport measurements indicate that the CDW order can be suppressed completely but no SC emerges yet under high pressures up to 11 GPa\textsuperscript{25}. Unlike AV\textsubscript{3}Sb\textsubscript{5} systems, there are two kagome sheets per unit cell separated by alternating ScSn\textsubscript{2} and Sn\textsubscript{2} layers in ScV\textsubscript{6}Sn\textsubscript{6}. Among previous RV\textsubscript{6}Sn\textsubscript{6} (R = Y, Gd-Tm, and Lu) with interesting f-orbital magnetism, no vanadium-driven order has been observed to date\textsuperscript{26,27}. The transport behaviors and the filling of the vanadium d-orbital bands are similar to AV\textsubscript{3}Sb\textsubscript{5}, the structural motif ScV\textsubscript{6}Sn\textsubscript{6} provides an optimum platform for further comprehending the origin of CDW in the kagome lattices.

It is very essential to get insights into the electronic band structure across the phase transition by varieties of spectroscopy techniques. Up to now, no angle resolved photoemission spectroscopy and scanning tunneling microscopy results have been reported yet. Optical spectroscopy are powerful and sensitive for detecting the bulk electronic states of solids. So it is significant to uncover the underlying physics of the phase transition by the infrared study.

In this work, we have successfully grown shiny hexagonal single-crystalline ScV\textsubscript{6}Sn\textsubscript{6} and characterize its basic physical properties. A pronounced kink hysteresis of first-order phase transition type around 92 K has been confirmed in resistivity measurement. Similar to many CDW systems, below the transition temperature, the compound keeps metallic response with forming CDW modulation. To further understand this issue, we performed temperature-dependent optical spectroscopy on monocrystalline kagome metal ScV\textsubscript{6}Sn\textsubscript{6}. The measurement reveals a sudden reconstruction of band structure with specific loss of conducting carriers below T\textsubscript{c}. Moreover, no second-order charge density condensation related gap development is observed in the optical spectra. It is obvious that there are two different metallic states below and above the T\textsubscript{c}. The sudden change of electronic structure is entirely consistent with the characteristics of the first-order structural phase transition. Therefore we could elaborate that the mechanism of CDW formation is in the sense that it is not driven by the Fermi surface nesting in the ScV\textsubscript{6}Sn\textsubscript{6}. Compare to the well-studied AV\textsubscript{3}Sb\textsubscript{5} results, the opening of the CDW gap and some first-order phase transition features are observed in AV\textsubscript{3}Sb\textsubscript{5} at the same time, the behavior has distinct difference in ScV\textsubscript{6}Sn\textsubscript{6}. Our work have enriched the comprehensions for...
FIG. 1. Sample physical characterizations for the kagome metal ScV$_6$Sn$_6$. (a) Temperature-dependent ab-plane resistivity measurement, a kink hysterisis is evident near 92 K. Inset: an optical micrograph of ab plane of ScV$_6$Sn$_6$ single crystal on a 1mm grid (b) Room temperature powder XRD patterns of single-crystal and indexing. Inset: The full width at half maximum of (004) bragg peak is about 0.06°, indicating good quality of single crystal.

the CDW formation in the exotic kagome metal systems.

II. RESULTS AND DISCUSSION

The single crystals of ScV$_6$Sn$_6$ were synthesized by the Sn self-flux method using an atomic ratio of Sc:V:Sn = 1:6:40. High-purity scandium grains (99.99%, 1-5 mm), vanadium powders (99.9%, 200 mesh), and stannum shots (99.999%, 1-3 mm) were firstly loaded into a aluminium crucible in order. Then the crucible was loaded into a 20-mm diameter quartz-tube with silica wool and column. All loading processes were operated in a sealed argon-filled glove box. Then the quartz tube was sealed under high vacuum and slowly heated to 1150 °C in a furnace followed by a 20 h dwell, then cooled to 750 °C at a rate of 1 °C/h. Single crystals of ScV$_6$Sn$_6$ with hexagonal shiny facet (typical size of 2×2×0.5 mm$^3$, as shown in the inset of Fig.1 (a)) were obtained after eliminating Sn flux by high-speed centrifuging. The temperature-dependent resistivity was measured by a standard four-probe method with current direction along the ab plane. The cooling/warming rate was set as 1K/min. The measurement was performed in a Quantum Design physical property measurement system (PPMS). Good metallic behavior is observed in resistivity measurements (shown in Figure 1(a)) and a small resistivity value of about 150 μΩ·cm at 300 K. Similar to the kagome metal AV$_3$Sb$_5$ (A= K,Rb,Cs) family CDW systems, ScV$_6$Sn$_6$ remains metallic state at LT phase and the residual resistance ratio ($RRR = \rho_{300 \text{K}}/\rho_{2 \text{K}}$) is about 6.4. The resistivity curve shows a significant kink hysteresis at around 92 K (as shown in 1(a)) indicating that the phase transition is of the first order. X-ray diffraction (XRD) experiment results at ambient conditions are shown in Fig.1 (b). The seven distinct diffraction peaks of Fig.1 (b) can be indexed as (00L) of ScV$_6$Sn$_6$ (deriving from CIF files in literature). It can be seen that the full width at half maximum of the strongest (004) Bragg peak is only about 0.06° in the inset of Fig.1 (b), indicating the high quality of ScV$_6$Sn$_6$ single crystal. Chemical compositions measurements by energy dispersive spectroscopy (EDS) results show that the chemical atomic ratios are close to the standard 1:6:6 stoichiometric ratio (Sc:V:Sn ~ 1: 5.88 : 6.27). All the sample fundamental characterizations are identified with the previous report$^{24,25}$.

The as-grown hexagonal ab-plane optical reflectance measurements were performed on the Fourier transform infrared spectrometer Bruker Vertex 80V at near-normal incidence in the frequency range from 40 to 30000 cm$^{-1}$. The sample is attached to a copper cone to reduce stray light influence as possible. And an in-situ gold and aluminum evaporation coating technique is performed at 300 K with the purpose of getting the absolute reflectance $R(\omega)$. The temperature-dependent optical data were collected when the sample was warmed up to the target temperature. The main panel of Fig.2 (a) displays the reflectivity up to 5000 cm$^{-1}$ at five selected tem-
Temperatures below and above $T_s$. The inset displays the experimental reflectance spectrum up to 30000 cm$^{-1}$ at 300 K. At very low frequency spectrum region, $R(\omega)$ has high values and approaches unit at zero frequency limit, reflecting the metallic nature of the compound in the $R(\omega)$ spectra. The slope of damping rate is nearly linear until 2000 cm$^{-1}$ in the frequency-dependent reflectivity at high temperature (HT) phase. This similar optical response has once been observed in some high-temperature cuprate superconductors. From 300 K to 100 K, the features of $R(\omega)$ shows very minor changes as schematic. However, when the temperature drops just down the structural phase transition temperature at 92 K, the optical reflectivity $R(\omega)$ shows distinctly different behavior up to 5000 cm$^{-1}$. With further decreasing temperature, the change of spectral feature becomes very small again. Below $T_s$, at the very low frequency far-infrared range, $R(\omega)$ increases slightly and becomes flat, reflecting metallic dc conductivity enhancement and is in accord with the above transport measurement. In the meantime, two invariant weak suppression features near 550 cm$^{-1}$ and 1300 cm$^{-1}$ could be illustrated.

To get more straightforward information linking to the band structures and joint density of states, the real part of optical conductivity $\sigma_1(\omega)$ was obtained from $R(\omega)$ through Kramers-Kronig transformation in Fig.2 (b). The Hagen-Rubens relation and the x-ray atomic scattering functions were used for the low-energy/high-energy extrapolation of $R(\omega)$\cite{28}, respectively. The main panel of Fig.2 (b) depicts $\sigma_1(\omega)$ below 10000 cm$^{-1}$ at five selected temperatures, the inset depicts $\sigma_1(\omega)$ up to 30000 cm$^{-1}$ at 300 K. All spectra exhibit a pronounced Drude response whose peak centering at zero frequency. The Drude response can be seen as a typical characteristic of metals. In HT phase, the broad width of Drude peak indicates a large scattering rate of the itinerant carriers. Upon entering the LT phase, the spectral weight of portion Drude-type conductivity was suddenly removed and transferred to the high energy excitations. In addition three conspicuous peaks at 600 cm$^{-1}$, 1150 cm$^{-1}$ and 2400 cm$^{-1}$ are formed. Unlike conventional CDW order formation, the whole shape of conductivity spectra kept almost unchanged at 5 K, 40 K and 70 K. The overall spectral change reflects a significant band structure reconstruction behavior associated with the structural phase transition. In other words, the sample gets into a different metallic state after transition.

As we know, in many representative and conventional CDW systems such as rare-earth tri-telluride (RTe$_3$), LaAgSb\cite{29,30}, it could be clearly identified that the optical spectral continuous change develops only in the low energy region at low temperature. Formation of CDW energy gap reflects the core of second-order phase transition behavior. The generally called case-I factor of CDW condensate would cause continuous spectral weight transferring so as to produce some increasing peaks just above the energy gap in the conductivity. With temperature further dropping down away the CDW phase transition, the suppression features in the reflectivity become more pronounced. It is the widely-accepted optical traits for conventional CDW condensation and possible

FIG. 2. Temperature-dependent optical spectroscopy of the ab-plane of ScV$_6$Sn$_6$. (a) temperature-dependent optical reflectivity measurements below 5000 cm$^{-1}$. Inset: Large energy scale range of 50-30000 cm$^{-1}$ at 300 K. (b) temperature-dependent optical conductivity below 10000 cm$^{-1}$. Inset: Optical conductivity spectrum with large energy scale range of 50-30000 cm$^{-1}$ at 300 K.
related structural transition. Conversely, unlike CDW order continuous formation behavior, there could be unpredictable and entirely different electronic states/band structures below and above the transition for the purely first-order structural phase transition as observed in IrTe$_2$ and 1T'-TaTe$_2$ CDW systems before$^{31,32}$. Moreover, the line shape would be nearly irrelevant to the temperature variation in the optical spectra. As for the ScV$_6$Sn$_6$ case, we observed that there are no continuous changes in the spectra upon entering into the CDW formation phase. Instead, the spectra just change immediately below the $T_s$ and remain almost unchanged. Based on these results and analysis, we could ascribe the transition to the purely first-order nature without finding any traces of conventional CDW gap formation in optical study.

Noting that the measuring reflectivity at 30000 cm$^{-1}$ is somewhat high, about 0.45, the high-energy side extrapolation in Kramers-Kronig transformation would affect the integration results and conductivity values especially in the mid-infrared region. Actually, the low energy conductivity is nearly unaffected. In this work we are mainly focus on the spectral characteristics and change below/above the transition so the specific numerical value of the conductivity peaks has no impact on our discussions and conclusions.

In order to distinguish the different components of the electronic excitations and analyze the data more effectively, we use the classical Drude-Lorentz model to fit the optical conductivity. The general formula for the Drude-Lorentz model can be describe as

$$\sigma_1(\omega) = \sum_{i} \frac{\omega_{pi}^2}{4\pi} \frac{\Gamma_D}{\omega^2 + \Gamma_D^2} + \sum_{j} \frac{S_j^2}{4\pi} \frac{\Gamma_j \omega^2}{(\omega^2 - \omega_j^2)^2 + \omega^2 \Gamma_j^2}$$  \hspace{1cm} (1)$$

where $\omega_{pi}$ and $\Gamma_D$ are the plasma frequency and the scattering rate of each conduction band while $\omega_j$, $\Gamma_j$, and $S_j$ represents resonance frequency, the damping, and the mode magnitude of each Lorentz oscillator, respectively. The first term is Drude component, representing the sum contributions from the free conduction carriers. The second Lorentz component terms are used to describe the excitations across energy gaps and interband transitions. Then we found that just one Drude component could approximately reproduce the low frequency region conductivity. The general formula for the Drude-Lorentz model is reproduced by a Drude component ($D_1$) and two Lorentz oscillators ($L_1$ and $L_2$) at 300 K. Below the transition temperature, the Drude term became narrow and three more Lorentz oscillators ($L_3$, $L_4$, and $L_5$) are requisite to fit the curve. The solid curves in Fig. 3 (a) and (b) are the experimental measured $\sigma_1(\omega)$ at 5 K and 300 K, respectively. And the black dashed line through the data shows the sum results of the Drude-Lorentz component fitting. In addition, the Lorentz 1 is highly stable in spite of temperature variation, which accordingly comes from the high-energy interband transition.

Figure 4 presents the two major fitting parameters of the Drude component. With the temperature decreasing, the overall variation tendency of both plasma frequency ($\omega_{pi}$) and scat-
FIG. 4. The values of the temperature-dependent fitting parameters (a) plasma frequency and (b) scattering rate.

tering rate ($\gamma_d$) is decreasing, as depicted in Figure 4(a) and 4(b). Since the square of plasma frequency is directly proportional to the carrier densities, we can infer a portion of the free carriers are lost after transition. At the same time, scattering rate drops extremely sharply, explaining even better dc conductivity in the LT phase.

It is inspiring to compare the present optical spectroscopy results on ScV₆Sn₆ with the similar vanadium structural motif kagome metals AV₃Sb₅ (A=K,Rb,Cs). The opening of the CDW gap behavior is clearly observed in CsV₃Sb₅ below $T_{cdw} \approx 94$ K in optical study²²,³³. Due to the CDW gap formation, a prominent spectral-weight transfer from low to higher energy regions and the weight of the Drude component is reduced. The importance of saddle point nesting was proposed in driving the CDW instability in CsV₃Sb₅. By some other experiment techniques, some first-order phase transition features were also observed, ie. the sudden change of the ultrafast relaxation dynamics and absence of CDW amplitude mode³⁴,³⁵. In a word, first and second order phase transition behaviors were both observed in AV₃Sb₅. But ScV₆Sn₆ exhibits differently behaviors, we just observed a sudden band reconstruction behavior tightly related to the structural transition, the optical spectra almost overlap with imperceptible difference below the $T_s$. So we ascribe this behavior to the pure first-order structural transition similar to the IrTe₂, TaTe₂ and BaNi₂As₂³¹,³²,³⁶.

Optical study could provide crucial information about the origin of the structural transition³⁷–³⁹. Based on the above experiment results and discussions, we could almost rule out the conventional Fermi surface nesting as the driving mechanism for the structural phase transition. Under this scheme, it is prerequisite to observe gap development process at low temperature, just as some typical density-wave condensation driving systems, e.g., LaAgSb₂, Bi₂Rh₃Se₂, RTe₃ (R=rare earth metal) and titanium oxypnictide Na₂Ti₂X₂O (X=As, Sb) series²⁹,³⁰,³⁷,³⁸,⁴⁰. For the unique kagome lattice, it is expected that there are some exotic saddle points in the electronic structure. One possible hypothesis is that one saddle point is close to the Fermi energy, thus resulting sudden lattice instability and CDW appearance at low temperature. Apparently, more theoretical and experimental works are still indispensable to elucidate the driving nature of the structural phase transition in ScV₆Sn₆ detailedly.

III. SUMMARY

In summary, our measurements on single-crystalline ScV₆Sn₆ reveal that the compound undergoes q distinct first-order type phase transition and kept metallic. The optical spectra further uncover the features of band structural sudden reconstruction. Although some of the free carriers are removed across the transition, the dramatic reduction of scattering rates make even better metallic properties in the LT phase. No gradually gap-opening behavior is observed in spectra so we elaborate that the phase transition is of the first-order type and is irrelevant to the conventional CDW instability. Compared to the widely-studied motif AV₃Sb₅ (A=K,Rb,Cs) series, the nature of the phase transition is different. Our spectroscopy results on ScV₆Sn₆ would provide an important foundation for further investigation of the origin or driving force of the intriguing phase transition in the kagome
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