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Tuning charge-density wave order and superconductivity in the kagome metals KV$_3$Sb$_{5-x}$Sn$_x$ and RbV$_3$Sb$_{5-x}$Sn$_x$

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The family of AV$_3$Sb$_5$ (A = K, Rb, Cs) kagome metals exhibit chiral charge density wave (CDW) order followed by a superconducting state. Recent studies have shown the importance that band structure saddle points proximal to the Fermi energy play in governing these two transitions. Here we show the effects of hole-doping achieved via chemical substitution of Sn for Sb on the CDW and superconducting in both KV$_3$Sb$_5$ and RbV$_3$Sb$_5$, and generate a phase diagram. Lifting the $\Gamma$ pocket and van Hove singularities (vHs) across $E_F$ causes the superconducting $T_C$ in both systems to increase to about 4.5 K, while rapidly suppressing the CDW transitions.

INTRODUCTION

Structures with kagome nets inherently host electronic instabilities that lead to a variety of interesting phases, including topological insulators,[1] unconventional superconductivity,[2] and Weyl semimetal states [3]. The AV$_3$Sb$_5$ (A = K, Rb, Cs) class of kagome metals [4] show many of these unconventional states and are candidates to study the interplay between charge density wave (CDW) order and superconductivity (SC) [5–7]. Recently, the effects of making small changes to the electronic band structures on SC and CDW ordering have been studied computationally [8, 9] and experimentally by applying external hydrostatic pressure [10–13] and hole doping on various sites [14].

The electron pocket comprising Sb $p$ orbitals at $\Gamma$, and saddle points arising from $V \, d$-orbitals at $M$-points are regarded as being important to the SC and CDW states and consequently, understanding their behavior when subject to external perturbations such as pressure and chemical doping is important to understand. Recently, we reported the effect of hole doping in CsV$_3$Sb$_5$ with Sn substituting Sb, and observed a double superconducting dome that we attributed to the lifting of the $\Gamma$ pocket above $E_F$. The van Hove singularities (vHs) at the $M$ point are lifted with the substitution resulting in rapid suppression of the CDW transition [14]. While external applied pressure moves the $M$ saddle points away from $E_F$, hole-doping the systems moves the $\Gamma$ pocket and vHs points up through $E_F$ [8]. Despite these differences, it is interesting to note that the observed changes in SC and CDW are similar in both pressure and hole-doping studies. In CsV$_3$Sb$_5$, two peaks in SC $T_C$ are observed with a suppressed and eventually disappearing CDW transition with both low applied pressure ($P < 5$ GPa) [11] and hole-doping on the Sb site [14]. Conversely, pressure studies have reported a single superconducting dome in KV$_3$Sb$_5$ and RbV$_3$Sb$_5$ [10, 12].

Here the effect of hole doping AV$_3$Sb$_5$ with in solid solutions with $A = K, Rb$ is presented. In both systems, only one superconducting dome is observed in contrast with CsV$_3$Sb$_{5-x}$Sn$_x$, although a similar CDW suppression is observed. The solubility limit of Sn in KV$_3$Sb$_5$ is the lowest in the family, with phase separation observed by $x = 0.30$. In contrast RbV$_3$Sb$_5$ supports up to $x = 0.70$ of Sn replacing Sb. While the differences in solubility can be explained by A cation size effects, the different SC and CDW behavior must be attributed to subtle differences in band structure. Recent optical measurements coupled with density functional theory (DFT) calculations have shown that the saddle points around $M$ are slightly rearranged between CsV$_3$Sb$_5$ and KV$_3$Sb$_5$ [8, 9], which may lead to the differences observed in superconductivity enhancement.

EXPERIMENTAL DETAILS

Powder samples of KV$_3$Sb$_{5-x}$Sn$_x$ and RbV$_3$Sb$_{5-x}$Sn$_x$ for $0 \leq x \leq 1$ were synthesized as described previously [14]. Structural analysis was performed via a Panalytical Empyrean laboratory x-ray powder diffractometer. A Hitachi TM4000Plus scanning electron microscope (SEM) was used to perform energy-dispersive X-ray spectroscopy (EDS). A Quantum Design Magnetic Property Measurement System (MPMS) was used to collect magnetization data and a Quantum Design Physical Property Measurement System (PPMS) Dynacool was used for resistivity measurements. To gain insight into the electronic states of all compounds, first-principles calculations based on density functional theory (DFT) within the Vienna ab initio Simulation Package (VASP) were performed [15, 16].

RESULTS AND DISCUSSION

AV$_3$Sb$_{5-x}$Sn$_x$ all adopt the parent hexagonal $P6/mmm$ structure at room temperature, with the V atoms making up an ideal kagome network. $^{121}$Sb nuclear quadrupole resonance (NQR) studies on
CsV₃Sb₅₋ₓSnₓ have shown that the Sn atoms preferentially occupy the Sb1 sublattice site in the kagome plane [14]. Due to the similarity in structure in all of the AV₃Sb₅ structures, we assume that the Sn atoms occupy the Sb1 sublattice for A = K, Rb as well. For KV₃Sb₅₋ₓSnₓ, polycrystalline samples were found to be single phase for x ≤ 0.25, while for RbV₃Sb₅₋ₓSnₓ, polycrystalline samples were single phase for x ≤ 0.7, at which point the limit of the solid solution was reached and secondary phases were observed in both families.

The powder diffraction data was fitted using the Pawley method to study changes in unit cell as a function of Sn content. Similar to the decreases observed in CsV₃Sb₅₋ₓSnₓ, a increases as c decreases with increasing Sn content in both A = K, Rb as seen in Fig. 1(b,e), while the volume is independent of Sn content (Fig. 1(c,f)). The solubility limit of Sn is clearly reached once the c/a ratio deviates from its linear trend (x ≈ 0.30 for KV₃Sb₅₋ₓSnₓ and x ≈ 0.70 for RbV₃Sb₅₋ₓSnₓ), and a secondary phase emerges in the powder diffraction data. EDS was performed on samples with a critical Sn content to confirm the nominal Sn content (Fig. 1(d, g)).

Single crystal KV₃Sb₅ has a superconducting Tₘ of 0.93 K[6]. Here, the Tₘ of polycrystalline KV₃Sb₅ is lower than 1.8 K, the lowest achievable temperature on the MPMS, but as Sn was incorporated, the superconducting transition temperature increases and can be detected by x = 0.03. Figure 2(a) shows the evolution of the superconducting transition up to x = 0.25, where Tₘ is at a maximum of 4.5 K. Beyond this Sn content, a secondary phase appears, so a suppression of superconductivity is not observed for a solid solution of KV₃Sb₅₋ₓSnₓ.

Electrical resistivity measurements of samples near the superconducting dome peak are shown in Figure 2(e).
FIG. 2. (a) The superconducting $T_C$ of $KV_3Sb_{5-x}Sn_x$ measured under a field of $H = 5$ Oe systematically shifts to higher temperature in compositions up to $x = 0.30$. The superconducting fraction is normalized to account for errors in mass and packing fraction so all data have a minimum of $-1$, the theoretical minimum. (b) $1/\chi$ for compositions $x \leq 0.05$ in $KV_3Sb_{5-x}Sn_x$ show the CDW $T^*$ decreases from 86 K to 59 K and disappears for $x \geq 0.05$. (c) The superconducting $T_C$ of $RbV_3Sb_{5-x}Sn_x$ measured under a field of $H = 5$ Oe systematically shifts to higher temperature in compositions up to $x = 0.40$. (d) $1/\chi$ for compositions $x \leq 0.10$ in $RbV_3Sb_{5-x}Sn_x$ show the CDW $T^*$ decreases and eventually disappears for $x \geq 0.10$. (e) Resistivity data for $KV_3Sb_{4.8}Sn_{0.2}$ and $RbV_3Sb_{4.6}Sn_{0.4}$ confirm the $T_C$ transitions and lack of CDW transitions for these higher Sn content samples.

The superconducting states are clearly observed as zero-resistivity conditions and the transitions at 4.25 K for $KV_3Sb_{4.8}Sn_{0.2}$ and 4.4 K for $RbV_3Sb_{4.6}Sn_{0.4}$ agree well with those seen in the magnetization data, while CDW transitions are not present. The residual resistance is much higher in $RbV_3Sb_{4.6}Sn_{0.4}$ and is even higher in $CsV_3Sb_{4.65}Sn_{0.35}$, suggesting an $A$-site dependence.

The effects of Sn-substitution on SC and CDW orders in $KV_3Sb_{5-x}Sn_x$ and $RbV_3Sb_{5-x}Sn_x$ are summarized in Figure 3. In both systems, the CDW ordering temperature is rapidly suppressed in a roughly linear fashion even with small amounts of hole doping and fully disappears before the maximum superconducting transition temperatures. The single dome nature of Sn-substituted $KV_3Sb_5$ and $RbV_3Sb_5$ is distinct from recent pressure studies that observe a double superconducting dome, with a sharp increase in $T_C$ at very low applied pressures and a second dome emerging at much higher pressures [10, 12]. Moreover, Du et al. report the persistence of charge ordering at the first superconductivity peak. The differences between external pressure effects and hole-doping can be attributed to the opposite effects that these changes have to the band structures of $AV_3Sb_5$ compounds [8].

Due to size considerations, the solubility limits of Sn in $KV_3Sb_5$ and $RbV_3Sb_5$ are much lower than in $CsV_3Sb_5$. However in all of these systems, the changes in electronic structure for the compositions of interest can be extrapolated by computing band structures of substitution one $Sb$ atom for an Sn atom within the kagome plane and out of the kagome plane. Figure 4(a) and (d) shows the band structure of undoped $KV_3Sb_5$ and $RbV_3Sb_5$, respectively, with the range of achievable Fermi levels with the loss of 1 electron per unit cell indicated in gray. Figure 4(b) and (e) show a hypothetical structure where the $Sb1$ lattice is fully substituted for Sn. The shifts in band structure are
The changes in band structure for Sn substitution on the Sb1 sublattice in KV₃Sb₅Sn and RbV₃Sb₅Sn at first sight, appear to be very similar to those in CsV₃Sb₅Sn. However, subtle differences are evident that lead to distinct superconducting behavior. A closer examination of the saddle points around \( E \) reveals that the irreducible representations of the two points are not the same for \( A = \text{K, Rb and Cs} \) \cite{8, 9}. As a consequence of the saddle point inversions, bands cross near \( E_F \) in CsV₃Sb₅ but not in KV₃Sb₅.

Hydrostatic pressure studies for AV₃Sb₅ reveal that CsV₃Sb₅ shows two superconducting \( T_C \) peaks \cite{11} but only one peak for KV₃Sb₅ and RbV₃Sb₅ \cite{10, 12} at low applied pressure (less than 5 GPa). Labollita et al. report that the vHs under hydrostatic pressure move down in energy away from \( E_F \), and moreover the vHs points closest in energy to \( E_F \) shift uniformly (vHs1 and vHs2). Conversely, these points move up closer to \( E_F \) with hole doping, so it is interesting that similar effects are seen in the superconducting and charge density wave ordering with hydrostatic pressure and hole doping. In KV₃Sb₅, the energy of vHs2 barely changes with increased hole doping, but vHs1 increases in energy until it crosses vHs2 at a critical hole concentration. The energies of vHs2 and vHs1 have similar behavior in RbV₃Sb₅ but cross at a lower hole concentration in RbV₃Sb₅, with vHs2 starting at a slightly higher energy than vHs1 in pristine RbV₃Sb₅ and staying mostly constant with hole doping, but vHs1 increasing in energy. The energies of the two vHs points are much closer in RbV₃Sb₅ than in KV₃Sb₅. Finally, the energies of vHs1 and vHs2 are inverted in CsV₃Sb₅ (with vHs1 higher than vHs2) and both steadily increase with hole doping and never cross \cite{8}. As holes are introduced to the system and the \( \Gamma \) pocket and vHs \( M \)-points are pushed up through \( E_F \), the different band crossings for the K and Rb systems versus Cs may lead to single dome rather than double dome superconductivity behavior.

The progressions of superconducting \( T_C \) and CDW temperature \( T^* \) is plotted as a function of Sn composition for KV₃SbₓSnₓ and RbV₃SbₓSnₓ. In the potassium version, the solubility limit of Sn is reached before a full superconducting dome is achieved, but the suppression of CDW \( T^* \) is still fully realized. RbV₃SbₓSnₓ shows a single superconducting dome before the solubility limit is reached, with an accompanying suppressed CDW by \( x = 0.1 \).

similar to those seen in CsV₃Sb₄Sn, with the \( \Gamma \) pocket and \( M \)-point vHs lifted above the Fermi level. The calculated band structures for this structure overall suggests a rigid band shift model. Band structures for Sn substituted in the Sb2 sublattice are plotted in Figure 4(c) and (f) and show significant reconstructions at multiple points, including \( K \), \( L \), and \( H \).

CONCLUSION

Hole-doping achieved via substitution of Sn on Sb sites in KV₃Sb₅ and RbV₃Sb₅ reveals similar phase diagrams consisting of a single SC dome and quickly suppressed CDW order. The V-orbital vHs are pushed up through \( E_F \) with hole-doping and likely lead to the suppression of CDW order. The \( \Gamma \) pocket from the Sb \( p_z \) states is quickly lifted above \( E_F \) and contributes to the enhanced superconducting \( T_C \). In these two systems, CDW and SC order seem to be more directly in competition than in CsV₃Sb₅, although further theoretical studies are important to further clarify the differences between the three systems, especially between KV₃Sb₅ and RbV₃Sb₅. Small changes in electron count in KV₃Sb₅ and RbV₃Sb₅ achieved via Sn substitution dramatically affect the SC and CDW orders.
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