

Effect of chemical doping on heterostructured Fe-based superconductor $\text{Sr}_2\text{VO}_3\text{FeAs}$

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(Received 23 February 2018; revised or reviewed 23 March 2018; accepted 24 March 2018)

Abstract

Phase diagrams of electron- and hole-doped $\text{Sr}_2\text{VO}_3\text{FeAs}$ are investigated using Co and Mn substitution at Fe site. Metallic nature survives only for Co (electron) doping, not for Mn (hole) doping. The conductivity of $\text{Sr}_2\text{VO}_3(\text{Fe},\text{M})\text{As}$ ($\text{M}=\text{Mn},\text{Co}$) is sensitive to the structural modification of FeAs microstructure rather than carrier doping. This finding implies that the FeAs layer plays a dominant role on the charge conduction, thus the SrVO_3 layers should be considered as an insulating block. Also, we found that the superconductivity is rapidly suppressed by both dopants. This result is different from the conventional behavior that superconductivity is induced by doping in the most of Fe pnictides. Our finding strongly supports the uniqueness of $\text{Sr}_2\text{VO}_3\text{FeAs}$ among the Fe pnictide superconductors.

Keywords: Fe based superconductor, chemical doping, $\text{Sr}_2\text{VO}_3\text{FeAs}$

1. INTRODUCTION

Since the discovery of Fe-pnictide superconductors in 2008 [1], various types of structure of Fe-pnictide superconductors have been reported, such as “111”-type AFeAs ($\text{A} = \text{Li}, \text{Na}$) [2], “122”-type AFe_2As_2 ($\text{A}=\text{alkaline}$ or alkaline-earth metal) [3,4], “1111”-type ReOFeAs ($\text{Re} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ or Gd) [1,5,6] and “21322”-type $\text{Sr}_2\text{TMO}_3\text{FeAs}$ ($\text{TM}=\text{transition metal}$) [7,8]. They share the common “FeAs” layers, in which most of the interesting physical phenomena are observed [9]. They are known to have common characteristics regardless of the type of crystal structure. Usually the parent phase, C_2 -type antiferromagnetic order (AFM), is suppressed by chemical doping or physical pressure, and eventually the superconducting state is induced near the quantum critical point of the C_2 -AFM order.

Compared to other Fe-pnictide superconductors, $\text{Sr}_2\text{VO}_3\text{FeAs}$ exhibits several unusual properties and thus holds a unique position. $\text{Sr}_2\text{VO}_3\text{FeAs}$ has complex heterostructure consisting of $[\text{SrFeAs}]^{+1}$ superconducting layers and $[\text{SrVO}_3]^{-1}$ layers [7,8,10]. These heterostructure and their interfacial interaction are found to be important for the unusual C_4 symmetric electronic orders [8] coexisting with superconductivity. Furthermore $\text{Sr}_2\text{VO}_3\text{FeAs}$ shows superconductivity, even without doping [7,8], which can be considered as a model system for studying how various phases including superconducting phase in the correlated heterostructure are stabilized or modified by chemical doping or pressure. So far, however, systematic doping studies on $\text{Sr}_2\text{VO}_3\text{FeAs}$ has been rarely done [11,12], partly because of the difficulty of synthesizing good quality samples.

Here we report the effect of Fe-site substitution for $\text{Sr}_2\text{VO}_3\text{FeAs}$ with Mn and Co. For Mn doping, the system turns into the insulating phase with the doping level larger than 10% , while system remains in a metallic phase with Co doping up to 25%. These results confirm that the $[\text{SrVO}_3]^{-1}$ layer is insulating, due to strong correlation, consistent with ARPES results. Furthermore, we found that with Co doping, both the superconducting and the C_4 symmetric electronic order are suppressed, indicating possible intimate connection between them.

2. EXPERIMENTAL DETAILS

For Fe-site substitution, polycrystalline samples of doped $\text{Sr}_2\text{VO}_3\text{FeAs}$ were synthesized by conventional solid reaction. The starting materials include Co and Mn powder with stoichiometric ratio were pressed into a pellet and sealed in an evacuated quartz tube. All works were done in a glove box filled with ultra-purity Ar (99.9999 %) gas (the H_2O and O_2 contents are both below 0.1PPM). The sealed sample was sintered in furnace at 1150 °C for 40 hours, and then cooled down with a rate of 100 °C/h to the room temperature. Chemical analysis on the as-synthesized sample were done by EDS analysis of FE-SEM (Field Emission Electron Scanning, Philips Electron Optics B.V) instrument. Phase identification and crystal structure investigations were carried out using D/MAX-2500/PC (Rigaku) equipment with 18kW Cu target with Ni filter for the grounded powder sample. Resistivity measurement were done using a conventional 4-probe technique on PPMS (Physical Property Measurement System, Quantum Design).

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3. RESULTS

3.1. X-ray diffraction

Figure 1 and 2 show XRD patterns of Mn and Co doped $\text{Sr}_2\text{VO}_3\text{FeAs}$ polycrystalline samples, respectively. For un-doped $\text{Sr}_2\text{VO}_3\text{FeAs}$, $\text{Sr}_2\text{CuO}_3\text{GaS}$ -type tetragonal structure with the space group of $P4/nmm$ is a main phase (95.34 %), with minute impurity phases of Sr_2VO_4 (1.49 %) and FeAs (3.17 %). Such impurity phases might be reduced by optimizing stoichiometry ratio of the starting materials or sintering sequence. The lattice parameters of $\text{Sr}_2\text{VO}_3\text{FeAs}$ ($x=0$) are estimated to be $a = b = 3.933250(12)$

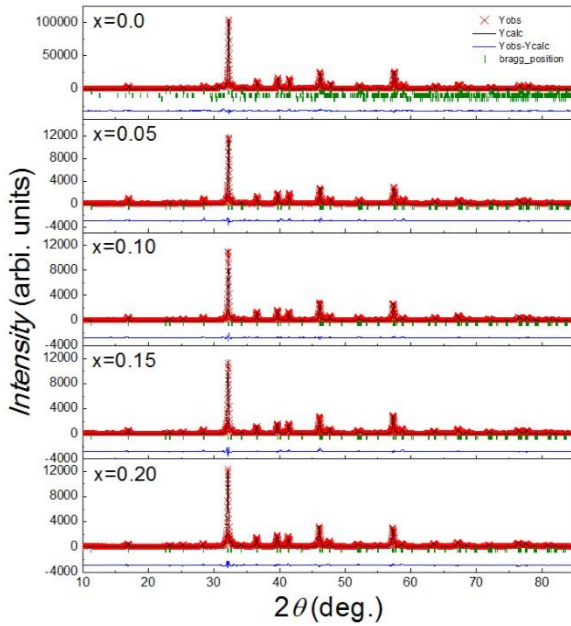


Fig. 1. Rietveld refinement patterns of $\text{Sr}_2\text{VO}_3(\text{Fe}_{1-x}\text{Mn}_x)\text{As}$ compound with various Mn doping ratio.

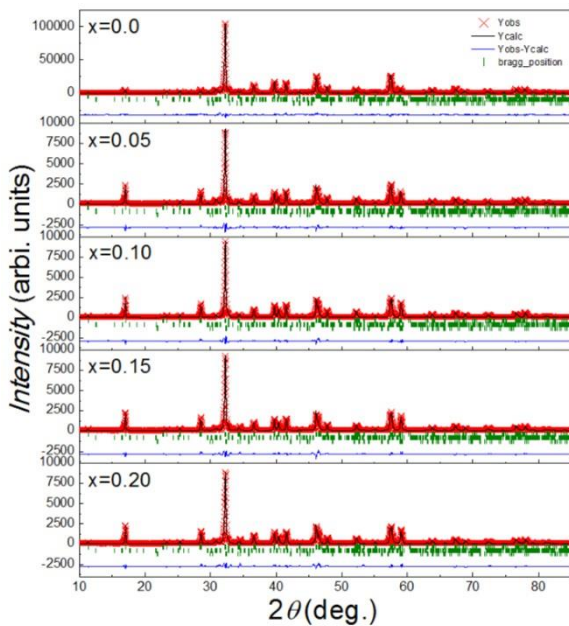


Fig. 2. Rietveld refinement patterns of $\text{Sr}_2\text{VO}_3(\text{Fe}_{1-x}\text{Co}_x)\text{As}$ compound with various Co doping ratio.

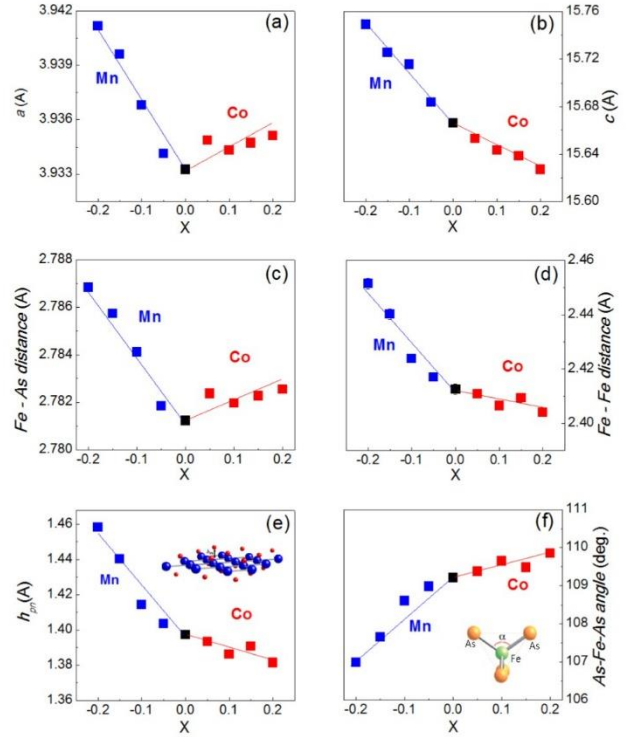


Fig. 3. Structural parameters of $\text{Sr}_2\text{VO}_3(\text{Fe}_{1-x}\text{M}_x)\text{As}$ ($\text{M}=\text{Mn},\text{Co}$) as function of Mn/Co doping ratio. (a) a parameter (b) c parameter (c) Fe-As distance (d) Fe-Fe distance (e) h_{pn} - height between Fe and As (pnictogen layer) and (f) As-Fe-As angle (Alpha angle). All parameters are estimated by Reitveld analysis.

Å and $c = 15.6664 \text{ Å}$ (volume = 242.36 Å^3), which is consistent with previous report ($a = b = 3.9302 \text{ Å}$, $c = 15.6664 \text{ Å}$) [7]. For Mn-doped sample ($x=0.2$), the lattice constants are estimated to be $a = b = 3.941183 \text{ Å}$ and $c = 15.7489 \text{ Å}$ (volume = 244.63 Å^3). For Co-doped sample ($x=0.2$), the lattice constants are $a = b = 3.935131 \text{ Å}$ and $c = 15.6271 \text{ Å}$ (volume = 241.98 Å^3). Compared to the parent compound $\text{Sr}_2\text{VO}_3\text{FeAs}$, increase (decrease) of the lattice volume upon Mn (Co) doping indicates a successful chemical substitution.

More detailed doping dependence of lattice parameter is shown in Fig. 3. Mn (Co) doping induces an obvious increase (decrease) in the c -axis lattice while the a -axis slightly increase. Not only the lattice parameter, but also the microstructure of FeAs tetrahedron is modified by Mn(Co) doping [13]. Figures 3 (c)-(f) show some structural parameters which describe FeAs tetrahedron structure. For Mn doping, the pnictogen height becomes longer and the As-Fe-As angle becomes smaller. This means that the FeAs layer is thickened due to Mn^{2+} ion (0.66 Å), which is bigger than Fe^{2+} ion (0.63 Å). When Fe-site is substituted by Co^{2+} (0.63 Å), which is smaller than Fe^{2+} ion, FeAs microstructure was changed in the opposite direction compared with Mn doping. Such a change of FeAs microstructure can modify the hopping path and the conductivity of FeAs layer. For example, increase of the Fe-As distance and decrease of As-Fe-As bond angle can reduced the hopping. In fact, insulating behavior was reported in Mn doped samples in other pnictides [13].

3.2. Resistivity of doped $\text{Sr}_2\text{VO}_3\text{FeAs}$

Figure 4 (a) and (b) shows temperature dependence of the normalized electrical resistivity in zero magnetic field for Mn and Co doped $\text{Sr}_2\text{VO}_3\text{FeAs}$, respectively. One can clearly notice that the temperature dependent resistivity shows systematic change with increase of doping level for both Mn and Co cases. Upon Co doping, the system becomes more metallic with reduction of T_c , similar to the behavior of over-doped Fe-pnictide. Here, the T_c is defined as the temperature of the onset of superconductivity. For Mn doping, the resistivity shows an insulating behavior with a rapid suppression of the superconductivity. These results are quite similar to Co- and Mn-doped SrFe_2As_2 as well as other Fe-site doped Fe-pnictide superconductors, suggesting that conducting properties are mainly determined by the $[\text{SrFeAs}]^{+1}$ layers rather than $[\text{SrVO}_3]^{-1}$ layers. In particular, the insulating behavior in the Mn-doped $\text{Sr}_2\text{VO}_3\text{FeAs}$ strongly suggests that the $[\text{SrVO}_3]^{-1}$ layer does not contribute to the electrical conduction, because it has been well-known that the FeAs layers become insulating when Mn is substituted at the Fe-sites. This finding is consistent with previous ARPES studies [14,15].

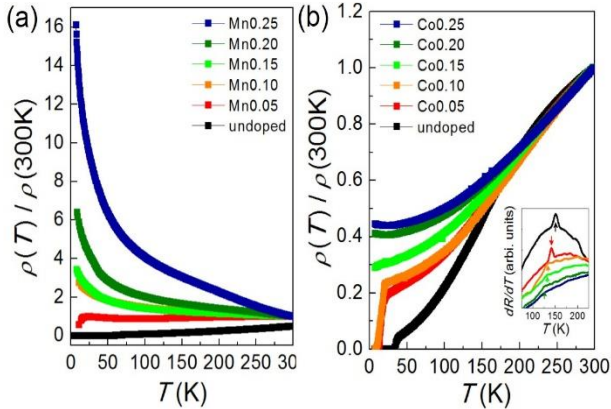


Fig. 4. Temperature dependence of normalized resistivity of (a) $\text{Sr}_2\text{VO}_3(\text{Fe}_{1-x}\text{Mn}_x)\text{As}$ and (b) $\text{Sr}_2\text{VO}_3(\text{Fe}_{1-x}\text{Co}_x)\text{As}$.

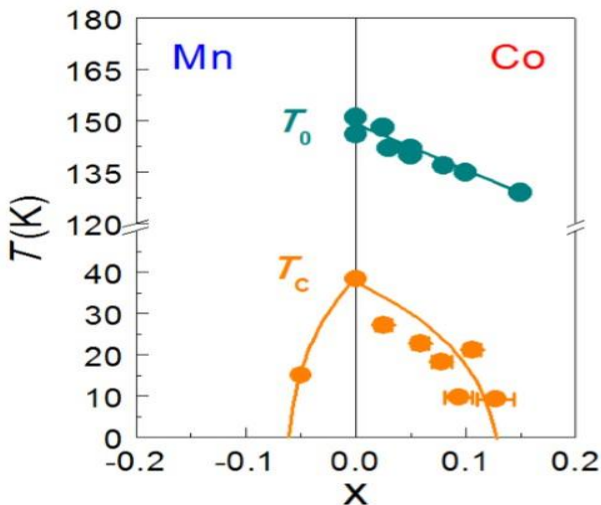


Fig. 5. A phase diagram of $\text{Sr}_2\text{VO}_3(\text{Fe}_{1-x}\text{M}_x)\text{As}$ ($\text{M}=\text{Mn}, \text{Co}$) as function of doping ratio

In temperature dependence of resistivity, we found another resistivity anomaly in addition to superconducting transition. For un-doped sample ($x=0$), a weak but clear resistivity anomaly is observed at $T_0 \sim 155$ K, which is estimated from the peak of the temperature derivative of resistance as shown in the inset of Fig. 4 (b). This finding is consistent with our previous work using single crystalline sample [8]. Upon Co doping at the Fe sites, the resistive anomaly at T_0 rapidly shifts to lower temperatures and becomes broader. However, in case of Mn doping, the anomaly was smeared out and therefore could not be observed.

Figure 5 shows a summarized phase diagram. The superconductivity was fully suppressed by both doping. While the superconductivity survives up to 15 % of Co doping, it is much rapidly suppressed for Mn doping. Such doping dependence of superconductivity is uncommon in Fe pnictide superconductors. Usually, superconductivity is induced by doping in the most of Fe pnictides. The unusual doping dependence in $\text{Sr}_2\text{VO}_3\text{FeAs}$ can be attributed to modification of FeAs microstructure. Based on the numerous studies on Fe pnictides, it has been known that T_c is maximized when As-Fe-As angle approaches to 109.4° forming a regular FeAs_4 tetrahedron [16]. The As-Fe-As angle in the un-doped sample is close to 109.4 degrees as shown in Fig. 3. Upon doping, the T_c tends to decrease as the As-Fe-As angle gradually deviates from optimal angle range. More interestingly, T_0 phase transition has a strong correlation with T_c . This is in obvious contrast to other Fe pnictides where the superconductivity induced by the suppression of normal electronic states. This finding suggests that the superconducting state in $\text{Sr}_2\text{VO}_3\text{FeAs}$ is strongly affected by its normal electronic state, but this can only provide limited information. Therefore, in order to broaden our understanding of unusual phase diagrams of $\text{Sr}_2\text{VO}_3\text{FeAs}$, it is highly required to investigate the normal electronic phases like magnetic ordering at $T_N \sim 45$ K and orbital ordering at $T_0 \sim 155$ K using single crystal or thermodynamic tools.

4. SUMMARY

In summary, we investigated the effect of Mn and Co-doping on heterostructured $\text{Sr}_2\text{VO}_3\text{FeAs}$. We found that Mn-doped $\text{Sr}_2\text{VO}_3\text{FeAs}$ shows insulating behavior, whereas Co-doped $\text{Sr}_2\text{VO}_3\text{FeAs}$ becomes more metallic. This finding suggests that $[\text{SrVO}_3]^{-1}$ layer is insulating, consistent with APRES studies. The superconductivity is suppressed by both doping. This result is different from the general knowledge that superconductivity is usually induced by chemical doping and thus more researches are highly required.

ACKNOWLEDGMENT

This work was supported by SRC center for Topological Matter (No. 2011-0030785) and the Max Planck POSTECH/KOREA Research Initiative Program (No.

2016K1A4A4A01922028) through NRF in Korea.

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