Superconducting transition temperatures in the electronic and magnetic phase diagrams of Sr$_2$VFeAsO$_3$–$\delta$, a superconductor

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Abstract

We elucidate the magnetic phases and superconducting (SC) transition temperatures ($T_c$) in Sr$_2$VFeAsO$_3$–$\delta$ (21113V), an iron-based superconductor with a thick-blocking layer fabricated from a perovskite-related transition metal oxide. At low temperatures ($T < 37.1$ K), 21113V exhibited a SC phase in the range $0.031 \leq \delta \leq 0.145$ and an antiferromagnetic (AFM) iron sublattice in the range $0.267 \leq \delta \leq 0.664$. Mixed-valent vanadium exhibited a dominant AFM phase in $0.031 \leq \delta \leq 0.088$, and a partial ferrimagnetic (Ferri.) phase in the range $0.124 \leq \delta \leq 0.664$. The Ferri. phase was the most dominant at a $\delta$ value of 0.267, showing an AFM phase of Fe at $T < 20$ K. Increasing the spontaneous magnetic moments reduced the magnetic shielding volume fraction due to the SC phase. This result was attributed to the magnetic phase of vanadium, which dominates the superconductivity of Fe in 21113V. The $T_c$–$\delta$ curve showed two maxima. The smaller and larger of $T_c$ maxima occurred at $\delta = 0.073$ and $\delta = 0.145$, respectively; the latter resides on the phase boundary between AFM and the partial Ferri. phases of vanadium. 21113V is a useful platform for verifying new mechanisms of $T_c$ enhancement in iron-based superconductors.
Therefore, constructing the magnetic and electronic phase diagram of Sr$_2$VFeAsO$_{3-\delta}$ requires a systematic study of the chemical compositions and element-specific magnetic measurements of the family.

1. Introduction

1.1. Backgrounds of iron-based high-$T_c$ superconductors, $Ae_2M$Fe$Pn$O$_{3-\delta}$

The discovery of high-temperature iron-based superconductors in mixed anion layered compounds (MALCs) [1–5] has triggered the search for superconducting (SC) materials. Considerable attention has been devoted to the newly developed superconductors with Fe square lattices. In 2009, the $Ae_2$MFe$Pn$O$_3$ family of SC layered iron pnictides was reported (the so-called 21113 systems), characterized by a perovskite-type layered local structure of $Ae_2MO_3$, where $Ae$ denotes an alkaline-earth metal, $M$ denotes Sc, Ti, Cr, V or another transition metal and $Pn$ denotes P or As. The onset temperatures ($T^{\text{onset}}$) of the SC transitions of nominally synthesized Sr$_2$ScFePO$_3$ and Sr$_2$VFeAsO$_3$ are 17 K [6] and 37.2 K [7], respectively. However, several 21113 systems have been reported that they exhibit no SC phase unless $M^{3+}$ is substituted with Ti$^{4+}$ [8–15]. Other promising candidates for superconductivity applications are Sr$_2$Sc$_2$Fe$_2$As$_2$O$_5$ [16, 17]; a member of the so-called 32225 systems, and a homologous series of compounds [18, 19], which present perovskite-related blocking layers thicker than the 21113 systems. These backgrounds are detailed in section 1 of supplementary information (available online at stacks.iop.org/JPhysCM/31/115801/mmedia).

Amongst the 21113 compounds, Sr$_2$VFeAsO$_{3-\delta}$ is an attractive SC material for practical use because its large upper critical magnetic field ($\mu_0H_c^2$) [7, 20] is suitable for applications involving high magnetic fields. As shown in figure 1(a), the crystal structure of Sr$_2$VFeAsO$_{3-\delta}$ is a tetragonal lattice with the FeAs carrier-conducting layers sandwiched between the Sr$_2$VO$_{3-\delta}$ perovskite-related carrier-blocking layers. Sr$_2$VFeAsO$_{3-\delta}$ compounds with nominal chemical compositions, undergo SC transitions at $T^{\text{onset}} < 37.2$ K [7, 20–26] under ambient pressure and at $T^{\text{onset}} = 46.0$ K [21] under high pressure. Munevar et al. [26] and Hummel et al. [27] reported a quadrupole doublet in the $^{57}$Fe Mössbauer spectra (MS) of SC Sr$_2$VFeAsO$_{3-\delta}$ at 1.5–300 K, indicating no spontaneous magnetic moment in the Fe sublattice. In contrast, the $^{57}$Fe Mössbauer spectrum of normally conducting Sr$_2$ScFeAsO$_3$ [26] exhibits sextet lines, indicating a finite internal magnetic field induced by the magnetic moments of the Fe sublattice, whereas that of Sr$_2$CrFeAsO$_3$ [28] shows substantial broadening at 4.2 K, which can be fitted to various internal magnetic fields. The $^{57}$Fe MS of Sr$_2$MFeAsO$_3$ ($M$ = Sc, Cr) suggest a magnetic phase of the Fe sublattice in Sr$_2$VFeAsO$_{3-\delta}$ but current reports are controversial [20, 22–24, 26, 27, 29]. Therefore, constructing the magnetic and electronic phase diagrams of Sr$_2$VFeAsO$_{3-\delta}$ requires a systematic study of the chemical compositions and element-specific magnetic measurements of the family.

1.2. Overview of the present study on SC Sr$_2$VFeAO$_{3-\delta}$

In this study, polycrystalline Sr$_2$VFeAsO$_{3-\delta}$ samples containing secondary phases were prepared with various $\delta$. In general, verifying the oxygen contents in polycrystalline samples containing second phases is a difficult task. Moreover, the transport properties and magnetism in such polycrystalline samples cannot be ignored without reasonable assumptions. In the present study, the $\delta$ values are determined from the linear relationship between $\delta$ and the lattice volume $V$. The reliability of the $\delta$ estimates can be checked by the chemical shift values, defined by the peak positions of vanadium K-edge fluorescence (XRF) spectra, which indirectly quantify the oxygen contents in Sr$_2$VFeAsO$_{3-\delta}$. The obtained samples were characterised by x-ray diffraction (XRD), XRF, $^{57}$Fe Mössbauer spectroscopy [30] and thermal gas desorption. The SC and magnetic phase transition temperatures of the samples were clarified in resistivity ($\rho$) and magnetic moment measurements at various temperatures ($T$). Normally conducting samples with $0.267 \leq \delta \leq 0.664$ exhibited an antiferromagnetic (AFM) phase of Fe. The topological difference between the magnetic Fe phase and the SC phase is similar to those of other high-$T_c$ superconductors, including ReFeAsO$_{1-\delta}$ (F, H)$_x$ (Re: rare earth) [31, 32] and YBa$_2$Cu$_3$O$_{7-\delta}$ [33–35]. Meanwhile, samples in the $0.031 \leq \delta \leq 0.267$ and $0.124 \leq \delta \leq 0.664$ ranges exhibit a dominant and/or partial AFM phase of V and a partial and/or dominant ferrimagnetic (Ferri.) phase of the V, respectively. Our interpretations are supported by density functional theory (DFT) calculations in the magnetic phase of Sr$_2$VFeAsO$_{3-\delta}$ [23].

In the earlier reports [7, 20–27, 29], an electronic and magnetic phase of Sr$_2$VFeAsO$_{3-\delta}$ had been controversial due to an absence of a simplified assumption that determine chemical compositions of the polycrystalline samples based on analytical chemical approach; e.g. volume Vegard’s rules (VVR) [36]. Using analogy of the VVR, present study newly introduces a verifiable relation between lattice volume $V$ and intrinsic $\delta$ and successfully demonstrates element-specific electronic and magnetic phase diagram for Sr$_2$VFeAsO$_{3-\delta}$ (see figure 10).

The $T_c$ versus $\delta$ plot displays two maxima. The lower maximum coexists with the AFM phase of the V sublattice, and the higher maximum appears near the boundary between the AFM and the Ferri. phases of the V sublattice. In the $T_c$
versus δ plot, AFM phase of the Fe sublattice exists separately from the SC phase. Electronic and magnetic phase of the Fe sublattice is in accord to Goodenough’s empirical consideration ‘T-b diagram’ [37]. The present Tc versus δ plot, which is dominated by Fe 3d electrons and V 3d electrons, has updated the ‘T-b diagram’ on more complex electronic phases of d-electrons empirically. These results clarify a topology between the superconductivity and the magnetism in MALCs with perovskite-related magnetic oxide layers.

2. Experimental

2.1. Sample preparation and characterization

Polycrystalline samples were prepared by the two-step solid-state reaction process in a sealed silica tube. The starting materials were dehydrated SrO, FeAs, V2O5, and V. The dehydrated SrO was prepared by heating commercial Sr(OH)2·8H2O powder (Sigma Aldrich Japan Co. Ltd; 99.995 wt.% ) at 900°C for 10 h in air. The FeAs powder, was obtained by mixing Fe (Ko-jundo Chemical Laboratory; ≥99.99 wt.%) and As (Ko-jundo Chemical Laboratory; 99.9999 wt.%) in a stoichiometric ratio of 1:1 and by heating the mixture at 600 °C for 10 h in an evacuated silica tube. The FeAs were then mixed with the dehydrated SrO, V2O5 (Sigma Aldrich Japan Co. Ltd; 99.99 wt.%), and V (Sigma Aldrich Japan Co. Ltd; 99.9 wt.% ) in the formula Sr2VFeAsO3−δ. The resulting powder was pressed into a pellet. The last two procedures were carried out in an Ar-filled glove box (MIWA Mfg; O2, H2O ≤ 1 ppm). The pellet was loaded into an alumina boat, sealed in an evacuated silica tube and heated to 1050 °C–1300 °C at 30 °C h−1. After maintenance at the target temperature for 20 h, the pellet was slowly cooled to room temperature (RT). The sample surfaces were polished using with SiC-coated abrasive paper sheets (Sankyo Rikagaku Co. Ltd; grit nos. 400 and 1000). The phase purity and lattice constants of the resulting powders were examined by powder XRD (Rigaku; RINT2500Ultra18) using Cu Kα radiation from a rotating anode. The samples were scanned at RT, and the lattice constants were obtained by the least-squares fitting method. Rietveld refinement was performed by the RIETAN-PP-Venus program [38]. Our analysis procedures are summarized in section 2 of supplementary information. (see figures S1–S3).

The low temperature XRD (LTXRD) measurements were performed with synchrotron radiation at beamline 16-BMD of the advanced photon source (APS) in the Argonne National Laboratory (ANL). The measurements were carried out at 5 ≤ T ≤ 30 K and at 290 K using a diamond anvil cell in a cryostat. The lattice constants as functions of T (5–30 K) were obtained from the LTXRD patterns.

The oxygen contents and valence states of the vanadium ions in representative Sr2VFeAsO3−δ samples were examined by XRF using wavelength-dispersive x-ray spectrometry (WDX; Rigaku ZSX100e) and thermal gas desorption spectrometry. Our analysis procedures are summarized in section 2 of supplementary information (see figure S4).
to 5.5 T. The analysis is detailed in section 3 of supplementary information (see figure S5). The $^{57}$Fe MS, measured for $\delta = 0.124, 0.232, 0.237, 0.267, 0.509, \text{ and } 0.631$ samples, were obtained from 2.5 to 300 K by conventional equipment with a $^{57}$Co source [30]. The isomer shift (IS) values of each sample were determined relative to that of $\alpha$-Fe. Details are given in section 4 of supplementary information (figures S6 and S7).

2.3. Ab initio calculations for stability of the magnetic phases

The magnetic properties of Sr$_2$VFeAsO$_{3-\delta}$ were evaluated in conjunction with DFT calculations under the generalized gradient approximation (the Perdew, Burke and Ernzerhof approximation [39]), using Vienna ab initio simulation package (VASP) code [40, 41]. To describe the checkerboard-type antiferromagnetism in the vanadium layer reported by Nakamura et al [42], the unit cell was extended to a 32 atom $\sqrt{2} \times \sqrt{2} \times 1$ supercell (see figures 1(c)–(f)). The core valence interaction was treated within the projector-augmented wave scheme [43]. The plane-wave cut-off energy was 500 eV, and the Brillouin zone was sampled by a $3 \times 3 \times 1$ Monkhorst-Pack grid with $\sigma = 0.05$ eV. To account for the correlated 3d orbitals of vanadium, the calculations were performed at the DFT+$U$ [44] level. Following Nakamura et al [42], we set $U = 5.5$ eV and $J = 0.93$ eV. The experimental lattice constants were assumed in the calculations.

The oxygen-deficient structures ($\delta = 0.25$ and 0.50) were modelled by removing one or two 1-coordinated oxygen atoms from the supercell, as suggested by Suetin et al [45]. The internal coordinates were relaxed until the Hellmann–Feynman forces fell below $0.02$ eV Å$^{-1}$. The formation enthalpies in different magnetic configurations were evaluated by varying the initial magnetic moments on V and Fe.

3. Results

3.1. Crystallographic characterization

Figure 2 shows the powder XRD patterns of Sr$_2$VFeAsO$_{3-\delta}$ ($\delta = 0.124, 0.237$ and 0.509). Almost diffraction peaks are assigned to Bragg diffraction angles associated with the tetragonal Sr$_2$VFeAsO$_{3-\delta}$ phase, although several weak peaks could be attributed to secondary phases. The Rietveld refinement of the $\delta = 0.509$ sample revealed atomic coordination and an impurity phase content of ~7 vol.%. (see figure S3) The polycrystalline samples are dominated by the tetragonal Sr$_2$VFeAsO$_{3-\delta}$ phase. Meanwhile, the off-stoichiometry of oxygen and the appearance of secondary phases altered the chemical composition of the primary phase from the nominal. The δ values are determined from the lattice constants of representative samples. The XRD patterns of each sample are provided in figure S2 of supplementary information.
samples exhibited semiconductor-like negative values at $T \sim 10\,\text{K}$. The $\rho$-$T$ curves of the 0.664 samples showed anomalous maxima ($T_{\text{max}}$) at $T \sim 10\,\text{K}$. As the $\rho$ of the 0.267 samples was lower than that of the SC 0.031 samples and was absent in the normal conducting 0.031 samples, the bulk $T_c$ can be considered as the $T_c^{\text{mod}}$ (see table S3 in the supplementary information). In these samples, the bulk $T_c$ was less well clarified in the 0.204 samples with the SC trace than those of the SC 0.031 samples and was absent in the normal conducting 0.031 samples with no SC trace. Clearly, the $T_{\text{anom}}$ is associated with the appearance of SC phases.

### 3.4. Macroscopic magnetic properties

Figure 6(a) shows the temperature dependence of the spontaneous magnetization ($M_s$) in the $\delta = 0.124$, 0.204, 0.232, 0.237, 0.267, 0.509, 0.631 and 0.664 samples (where 1.8 $\leq T \leq 400\,\text{K}$). These curves reveal the magnetic phase transition temperatures $T_{\text{ferm}}$ of the samples, at which $M_s$ equals to 0.01 $\mu_B$ per formula unit (f.u.). The $M_s$ values of the 0.124--0.267 samples reached 0.011--0.53 $\mu_B$ (f.u.)$^{-1}$ at 1.8 K. The $M_s$ values of the 0.124 and 0.664 samples at 1.8 K were extrapolated by an empirical equation [46]. In the normally conducting samples, the $M_s$ and $T_{\text{ferm}}$ were maximized at $\delta = 0.267$ (figure 6(b)). At this composition, the $M_s$ was sufficiently large to verify intrinsic magnetism.
When the intrinsic $M_\text{f}$ is 0.01 $\mu_B$ (f.u.)$^{-1}$ or lower, it cannot be distinguished from extrinsic magnetic moments owing to the unknown ferromagnetic second phases. Several $T_{\text{fem}}$ maxima appear in the $T_{\text{fem}}$ vs. $\delta$ curve.

As shown in figure 6(c), the magnetic shielding volume fractions (SVFs) in the $\delta = 0.088$, 0.124 and 0.145 samples exceeded 10 vol.% at 1.8 K, whereas those of normal conducting samples (0.204 $\leq \delta \leq 0.237$) were below 10 vol.%.

Figure 5. (a) Electrical resistivities ($\rho$) of the Sr$_2$VFeAsO$_{3-\delta}$ (0.031 $\leq \delta \leq 0.664$) samples as functions of temperature ($T$). The $\delta$ value is indicated in each plot. The closed downward and open triangles indicate the onset temperatures of the bulk SC transition ($T_{\text{onset}}$) and the maximum temperatures of normal conductivity at 10–15 K ($T_{\text{on}}$) samples, respectively. The green upward triangles at $\approx$200 K indicate the temperatures of normal conductivity at 10 K.

3.5. $^{57}$Fe MS

Figure 7 shows the temperature dependence of the $^{57}$Fe MS of representative samples ($\delta = 0.232, 0.267$, and 0.509). The $^{57}$Fe MS of the other samples are presented in the supplementary information (figure S8). The $^{57}$Fe MS of each sample exhibit quadrupole doublet absorption lines at 300 K, indicating a paramagnetic (PM) phase of the Fe sublattice. The asymmetric doublet absorption lines derive from the anisotropic of crystal orientation [47] in Sr$_2$VFeAsO$_{3-\delta}$. The $^{57}$Fe MS of the $\delta = 0.232$ sample were fitted to a doublet pattern at 2.5 $\leq T \leq 300$ K with no internal magnetic field ($B_{\text{int}}$), indicating a PM Fe phase in this sample. In the $\delta = 0.124, 0.232$ and 0.237 samples, the PM Fe phase appeared at $T \geq 4.2$ K (see figure S6). The $^{57}$Fe MS of the $\delta = 0.267$ and 0.509 samples were fitted to a doublet pattern from 30 to 300 K. The absorption lines broadened at $T \sim 10$ K, indicating the presence of spontaneous magnetic moments in the Fe sublattice. The broad absorption lines clearly differed from the sextet split spectrum of antiferromagnetically ordered Fe sublattices, which typify the mother compounds of iron-based superconductors, e.g. LaFeAsO [30] and BaFe$_2$As$_2$ [48].
3.6. Correlations among thermal, electronic and magnetic properties

Figures 9(a) and (b) show the temperature dependences of the molar heat capacity ($C_{\text{mol}}$) and the excess contribution of the heat capacity ($C_{\text{ex}}$), obtained by subtracting the Debye phonon and Sommerfeld’s normally conducting contributions from $C_{\text{mol}}$. Figure 9(c) shows the differential length ($\Delta L$) of the lattice constants ($a$, $c$) in the normal conducting $\delta = 0.509$ sample. The $C_{\text{ex}}$ is attributable to a transition of the electronic and magnetic phases that predominantly contribute to the thermal properties of solids at low temperatures. The $C_{\text{ex}}$ was maximized at $T \approx 10$ K and decreased with increasing $T$, converging to zero at $T \approx 20$ K. In the $\delta = 0.509$ sample, the $C_{\text{ex}}-T$ correlated with the magnetic phase transition at the $T_N$ of Fe. The temperature dependences of the lattice constants $a$ and $c$, which are obtained from the LTXRD patterns, also show an anomalous kink at $\approx 10$ K (figure 9(c)). The anomalous kink is likely reflecting a local crystallographic structure transition in Sr$_2$VFeAsO$_3$. These results indicate a clear association between the anomalous kink in the $(a, c)$-T curves and $T_{\text{max}}$ in the $\rho$-T curve and a the lattice-formation-enthalpy in Sr$_2$VFeAsO$_3$.

3.7. Element specific electronic and magnetic phase diagrams

Figure 10 plots various temperatures ($T_N (\approx T_{\text{anom}})$, $T_{\text{ferri}}$ of V, $T_N$ of Fe, $T_{\text{max}}$, and $T_\gamma$) as a functions of $\delta$. Finite $\delta$ was inevitable in our samples. In the magnetic phase diagram of V in Sr$_2$VFeAsO$_3$, an AFM phase of V sublattice appeared in the $\delta = 0.031-0.267$ region (figure 10(a)). An AFM phase of V was earlier verified by Tatematsu et al [23]. The present samples exhibited a PM phase of the Fe sublattice from 20 to 300 K (figures 7 and S6). The $\delta = 0.124$, 0.204, 0.232, 0.237, 0.267, 0.509, 0.631 and 0.664 samples showed finite $M_S$ at $T < T_{\text{ferri}}$. The $T_{\text{ferri}}$ shows maximum at $T = 304$ K in the $\delta = 0.267$ sample and decreased as $\delta$ increased above 0.267. Both the AFM and Ferri. phases of V were observed in the $\delta = 0.124-0.267$ samples, indicating a phase-segregated magnetic state of the V sublattice. Such an inhomogeneous state is an intrinsic property of off-stoichiometric compounds. Indeed, the apparent mixed valence of V is an essential electronic state for a ferrimagnetic V phase in Sr$_2$VFeAsO$_3$.

The $\delta = 0.073$ and $\delta = 0.145$ samples possessed the optimum oxygen deficiencies that maximized the $T_S$. Sr$_2$VFeAsO$_3$ exhibited a bulk SC phase below the $T_{\text{end}} - \delta$ curve in the $0.031 \leq \delta \leq 0.145$ range and a normal conducting phase in the $0.204 \leq \delta \leq 0.664$ range, with SC-traces in the $0.204 \leq \delta \leq 0.237$ samples range. The electronic phase segregation, which is mainly induced by inhomogeneous chemical state, is consistent with the inhomogeneous magnetic V states in Sr$_2$VFeAsO$_3$ with $\delta = 0.124-0.267$. In the $0.031 \leq \delta \leq 0.237$ range, Sr$_2$VFeAsO$_3$ presented a PM...
phase of the Fe sublattice at 2 K. Meanwhile, the normally conducting samples ($\delta = 0.267, 0.509, \text{and} 0.631$) exhibited AFM phases of Fe at $T < \sim 20 \text{ K}$, indicating no coexisting SC and AFM phases of Fe in the prepared samples.

4. Discussions

4.1. Oxygen deficiencies and molecular (local) structures in the lattice

As shown in figure 3, the lattice volume of Sr$_2$VFeAsO$_{3-\delta}$ expanded with increasing $\delta$, as also observed in perovskite-type and perovskite-related compounds such as SrTiO$_{3-\delta}$ [53], YBa$_2$Cu$_3$O$_{7-\delta}$ [33], and Bi$_2$Sr$_1$Ca$_2$Cu$_3$O$_{10+\delta}$ [54]. Such lattice expansion probably characterizes the crystallographic properties of perovskite-related compounds. The average bond valence sum (BVS) [55] of VIII, VIV and VV in the $\delta = 0.509$ sample was 2.81, smaller than the average BVS reported by Cao et al [24]. The As–Fe–As bond angle ($\alpha$) in the FeAs layer of this sample was 106.43(9)$^\text{o}$ (see figure 1(b) and table S2 in the supplementary information), indicating that the FeAs$_4$ tetrahedron was distorted from the regular tetrahedron with $\alpha = 109.47^\text{o}$ [7, 24].

In the $T_{\text{max}}-\delta$ curve (figure 10), $T_{\text{max}}$ was assumed to equal the temperature of a local crystallographic transition, probed by the anomalous kinks in the $(a, c)-T$ curves of the $\delta = 0.509$ sample. The $T_{\text{max}}$ and $C_{\text{ex}}$ in this sample probably arose from the local crystallographic phase transition at 10 K (figures 5(a), 9(b) and (c)). A possible local crystallographic transition is consistent with $^{57}$Fe MS detailed in section 4 of the supplementary information. For a crystallographic site-specific analysis of 21113 with oxygen deficiencies, further neutron diffraction measurements and Rietveld refinement are required.

4.2. Formation enthalpy differences among magnetic phases in $\delta = 0$ sample

At the optimum $\delta$ in Sr$_2$VFeAsO$_{3-\delta}$, superconductivity was activated while the magnetic Fe phase was suppressed (figure 10). This result is consistent with Fermi surface nesting, a theoretical concept proposed by Nakamura et al [42], which suggests the emergence of an AFM phase of Fe. A similar relation between the AFM and SC phases of Fe has been reported in the 1111 compounds [2, 50]. The AFM phase of Fe may be understood as a spin density wave. The magnetic ground states of V and the Fe sublattices were quantified in DFT calculations of virtually defined Sr$_2$VFeAsO$_{3-\delta}$ supercells ($\delta = 0, 0.25 \text{ and} 0.50$) (figures 1(d)–(f)). Table 1 summarizes four different magnetic configurations of the $\delta = 0$ sample and

Figure 7. $^{57}$Fe MS of representative Sr$_2$VFeAsO$_{3-\delta}$ samples at different temperatures (indicated near the plots). (a) $\delta = 0.232$, (b) $\delta = 0.267$ and (c) $\delta = 0.509$. The solid lines are the fitted patterns to a wide distribution of internal magnetic fields. $^{57}$Fe MS are summarized with those of the other samples ($\delta = 0.124$ and $\delta = 0.631$) in figure S7 of the supplementary information.
the total energy of each configuration. The internal coordinates were fixed. The formation enthalpy differences (\(\Delta E\)) amongst the four configurations reflect the differences in their charge density distributions. The checkerboard-AFM phase (denoted c-AF) of V indicates that the neighboring magnetic V ions on the same layer always have opposite moments. We define the AFM ordering between two neighboring V layers with opposite moments as A-AF on V. A striped-AFM phase of Fe is defined as s-AF on Fe. In the s-AF phase, the magnetic ions on the same layer align in parallel rows, as proposed by Nakamura et al [42]. Concordant with their results [42], we referenced \(\Delta E\) to the most stable structures, c-AF on V and s-AF on Fe. The varying \(\Delta E\) indicates that several stable solutions were calculated for the same magnetic phase; the \(\Delta E\) of a magnetic phase are not unique. The lowest energies were 175 meV for [A-AF on V, PM on Fe] and 183 meV for [c-AF on V, PM on Fe], confirming that PM on Fe is not a ground state. In fact, s-AF was the most stable state of Fe. The minimum energy was 4 meV lower in [c-AF on V, s-AF on Fe] than in [A-AF on V, s-AF on Fe]. We concluded that the stability of A-AF and c-AF on V can be altered by slightly changing the chemical composition of Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\). Our results partially support the work of Nakamura et al [42]. The subtle differences between ours and Nakamura et al’s results are caused by the different exchange correlation potentials and/or initial conditions, such as the assumed magnetic moments of V and Fe. These discrepancies would be clarified in further computational analysis on a larger magnetic supercell of Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\).

4.3. Formation enthalpy differences among magnetic phases in \(\delta = 0, 0.25, 0.50\) samples

Consequent to the above analysis, we defined a ferromagnetic (FM) phase and a Ferri. phase of the V in oxygen deficient supercells. Table 2 summarizes several magnetic configurations of V and their \(\Delta E\)s in the \(\delta = 0, 0.25\) and 0.50 samples, assuming a fixed s-AF magnetic configuration of Fe. In this case, we relaxed the internal coordinates. The relaxation was within 0.02 nm along the c-axis and indiscernible along the other axes. Moreover, the relaxation trends were almost identical amongst the configurations. As shown in the first block of table 2, \(\Delta E\)s of several magnetic configurations on the V layer (the A-AF, FM, c-AFs and Ferri. phases) were very close. Under oxygen-deficient conditions (\(\delta = 0.25\) and 0.50), the magnitude of the magnetic moment of V clearly depended on \(\delta\) despite the \(\Delta E\) similarity. When oxygen is removed, V is deprived of its V–O bond in the supercell. Both the A-AF phase of V in the \(\delta = 0.25\) sample and the c-AF phase of V in the \(\delta = 0.50\) sample showed Ferri. phase behavior. Based on these results, we argue that the \(\alpha\) electrons are rather localized around V ions with magnetic moments from 1.9 \(\mu_B\) to 2.3 \(\mu_B\). When the magnetic moments of V are sufficiently different, the Ferri. phase of V might be stabilized by magnetic imbalance of the V sublattice. According to our calculations, the magnetic ground states of V in the virtual superlattice of Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\) were A-AF in the \(\delta = 0\) sample, Ferri. in the \(\delta = 0.25\) and 0.50 samples. The calculated stabilities of the magnetic V phases were consistent with the experimental results of the \(\delta \sim 0, -0.25\) and -0.50 samples. As shown in figures 6 and 10 and table 2, the \(\delta = 0.267\) sample yielded the largest spontaneous magnetic moment and the highest \(T_{\text{ferri}}\).

4.4. Comments on the possible mechanism of the \(T_{\text{N}}-\delta\) phase diagram and the enhancement of \(T_{\text{N}}\) near the ferrimagnetic phase of the vanadium

Magnetic Fe and magnetic V ions exist in a unit cell of Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\). The V sublattice of Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\) orders antiferromagnetically at \(\delta < 0.124\). A weak Ferrimagnetic ordered V sublattice of Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\) appears at \(\delta \geq 0.124\), and macroscopic spontaneous magnetic moment of the V reaches ~0.5 \(\mu_B\) (f.u.)\(^{-1}\) for \(\delta \sim 0.267\) sample (figure 6). Qian

![Figure 8. Electronic and magnetic properties of \(^{57}\)Fe in Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\). (a) Temperature (\(T\)) dependences of the ISs, QS and full width at half maximums (FWHMs) in the Sr\(_2\)VFeAs\(_O_3\)\(_{\delta-\epsilon}\) samples with \(\delta = 0.124\) (open circles), 0.232 (open squares), 0.237 (open triangles), 0.267 (closed triangles), 0.509 (red closed circles) and 0.631 (closed squares). The QS and FWHM values of the \(\delta = 0.267, 0.509\) and 0.631 samples are written only when the spectrum is a doublet. The black lines are the standard deviations. Insets are expanded views of the regular figures. Analytical details are provided in section 4 of the supplementary information. (b) Temperature (\(T\)) dependence of the square root of the mean squared amplitude of the internal magnetic field \(\sqrt{\langle B^2 \rangle}\) obtained from the internal magnetic field \(\langle B \rangle\) distributions of the \(\delta = 0.267, 0.509\) and 0.631 samples (which exhibited AFM ordering of the Fe sub-lattice at temperatures less than the Néel temperature \((T_{\text{N}}))\). The red dashed lines are fitted using the following equation [46]:

\[
\sqrt{\langle B^2 \rangle} = B_0 (1 - \frac{T}{T_{\text{N}}})^\alpha \quad \text{for} \quad 0 \leq \frac{T}{T_{\text{N}}} \leq 1
\]

where \(\alpha = 0.1\text{--}0.5\). Insets show distributed weights as functions of the \(B_{\text{int}}(W(B_{\text{int}}))\) in each sample at 4.2 K.]
et al observed Mott-insulating V 3d orbitals with Hubbard gap in SC Sr$_2$VFeAsO$_{1-x}$ using angle-resolved x-ray photoemission spectroscopy [56]. According to Qian et al’s report, the Mott-insulating V 3d orbitals are not hybridized with conducting Fe 3d orbitals around Fermi energy, although possible hybridization between the Fe 3d and the V 3d orbitals should be noted for $\delta \geq 0.124$ samples.

In general, an appearance of the high-$T_c$ SC phase is dominated by appearance of correlated electrons’ pairing mediated by both of a phonon [57] and another driving force [58]. The driving force has been quantitatively explained by so-called t–J model [59, 60] and spin-fluctuation mediated model [61, 62]. Each model have succeeded to demonstrate rational relation between bonding angles of FeAs$_4$ molecule and maximum $T_c$ in doped ReFeAsO [66]. Saito et al have focused on a discussion for iron-based superconductors’ anomalous robustness against various impurities and randomness [67]. Because the anomalous robustness is not explained enough by the spin-fluctuation-mediated model [63, 64], Saito et al introduced an orbital fluctuation mediated s-wave state for electrons’ pairing in iron-based superconductors. On the other hand, Yamase et al reported that an incommensurate magnetic order and d-wave superconductivity coexist in a 2D Hubbard model [68].

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d At low temperatures ($\gamma = 65.5(3)$ mJ K$^{-2}$ mol$^{-1}$ and $\beta = 0.52(1)$ mJ K$^{-4}$ mol$^{-1}$), $C_{ex}$ is calculated as $C_{ex} = C_{mol} - C_{low}$. $\Delta L$ is defined as changes of lattice constants ($a$ and $c$) from the values at 290 K.

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Figure 9. Temperature ($T$) dependences of molar heat capacity ($C_{mol}$) (a), excess contribution of heat capacity ($C_{ex}$) and lattice length change ($\Delta L$) (c) in Sr$_2$VFeAsO$_{1-x}$ ($\delta = 0.509$). The dashed line is the best-fits line of $C_{low} = \gamma T + \beta T^3$, where $\gamma$ and $\beta$ are the Sommerfeld coefficient and the lattice heat capacity coefficient, respectively, for the Debye heat capacity at low temperatures ($\gamma = 65.5(3)$ mJ K$^{-2}$ mol$^{-1}$ and $\beta = 0.52(1)$ mJ K$^{-4}$ mol$^{-1}$). $C_{ex}$ is calculated as $C_{ex} = C_{mol} - C_{low}$. $\Delta L$ is defined as changes of lattice constants ($a$ and $c$) from the values at 290 K.

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Figure 10. Element-specific electronic and magnetic phase diagrams of Sr$_2$VFeAsO$_{1-x}$ in terms of $\delta$ and $T$. (a) Magnetic phase diagram of V. Green closed triangles indicate the ferrimagnetic (Ferri.) phase transition temperatures, at which the spontaneous magnetic moment $M_S (T)$ is equal to 0.01 $\mu_B$ (f.u.)$^{-1}$. The green shaded area indicates a Ferri. phase. The blue open triangles indicate the AFM Néel temperatures ($T_N$), assuming that $T_N$ appears at $-T_{anis}$ (defined in figure 5), as reported by Tatematsu et al [23]. The blue shaded area indicates an AFM phase. The Ferri. and AFM phases overlap in the region of chemical inhomogeneity, which exhibits SC traces. (b) Electronic and magnetic phase diagrams of Fe in Sr$_2$VFeAsO$_{1-x}$. Red open circles indicate $T_{c}$ in bulk SC samples (see table S3 in the supplementary information). The small black lines in the plots are standard deviations. The red and blue shadowed area indicate the superconducting (SC) phase and AFM phase, respectively, and the blue closed squares indicate $T_{c}$ determined via $^{57}$Fe Mössbauer spectroscopy. Black downward triangles denote the $T_{c}$ Values of normally conducting samples, which are probably coupled with transitions in crystallographic local structure.
superconductors. Romer’s report indicated that appropriate amount of lattice defects and randomness possibly enhance the $T_c$ of iron-based superconductors.

In Sr$_2$VFeAsO$_{3-\delta}$, a weak ferrimagnetic V sublattice is observed in a SC sample which exhibits the highest $T_c \sim 37.1$ K at $\delta = 0.145$; i.e. the highest $T_c$ is observed in ‘so-called dirty SC state’. Provided that the Mott-insulating V 3d orbitals partially disintegrated in $\delta \geq 0.124$ samples, density of state of magnetic V 3d orbital should modulate the formation of Fermi surfaces and stability of correlated electrons’ pairing for superconductivity in Sr$_2$VFeAsO$_{3-\delta}$. Each theoretical model mentioned above might verify the mechanism for the maximum $T_c$ at $\delta = 0.078$ and 0.145 in figure 10.

5. Conclusions

We measured the electrical resistivities, magnetic properties and $^{57}$Fe MS of well-characterized polycrystalline Sr$_2$VFeAsO$_{3-\delta}$. DFT calculations support several magnetic phases in the V sublattice. Assuming linearity between $\delta$ and the lattice volume, we found that changing $\delta$ altered $a$–$\delta$ and $c$–$\delta$ curves. Bulk superconductivity was observed in the samples with $0.031 \leq \delta \leq 0.145$ samples. In the range $0.204 \leq \delta \leq 0.664$, the samples were normally conducting at $T > 2$ K, although SC traces were observed in the range $0.204 \leq \delta \leq 0.237$. These SC-traces were mainly attributable to chemical phase segregation. The highest $T^{\text{max}}_c$ and $T^{\text{ind}}_c$ were observed at 37.1 K and 34.1 K respectively, in the $\delta = 0.145$ sample. A spontaneous magnetic moment ($M_S$) of V appears in the 0.124 $\leq \delta \leq 0.631$. $M_S$ exhibits a maximum value $\sim 0.5 \mu_B$ (f.u.)$^{-1}$ in the $\delta = 0.267$ sample. The 0.124 $\leq \delta \leq 0.631$ samples exhibit a wide range of magnetic V transition temperatures (25–308 K). The $^{57}$Fe MS of Sr$_2$VFeAsO$_{3-\delta}$ verified PM phase in the Fe sublattice of the SC $\delta = 0.124$ sample and in the normally conducting samples with $\delta = 0.232$ and 0.237. The AFM phases of Fe appear at $T < 16.2(4)$ K, 19.2(4) K and 23.3(4) K in the $\delta = 0.267$, 0.509, and 0.631 samples, respectively. According to our DFT calculations, the stable AFM phase of V can be altered by varying $\delta$ (because the formation enthalpies of the various magnetic phases are quite similar); moreover, the Ferri. phase of V is stable when $\delta = 0.25$ and 0.50 samples. Based on these results, we constructed an electronic and magnetic phase diagram of Sr$_2$VFeAsO$_{3-\delta}$ with respect to $\delta$. This phase diagram verified the lack of coexisting AFM and SC phases in the Fe sublattice, although the maximum $T_c$ was raised near the AFM-Ferri. phases boundaries of V. The magnetic and valence states of V indirectly dominate the $T_c$ of Sr$_2$VFeAsO$_{3-\delta}$. Through this phase diagram, we can better understand the chemical compositions that optimise the superconductivity of iron-based MALC and thus develop mechanisms for enhancing $T_c$ in multinary transition metals-based MALCs, which are promising materials for SC applications under high magnetic fields.

This article contains supplementary information online referring to [71–93].

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