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Self-doping effect and successive magnetic transitions in superconducting Sr$_2$VFeAsO$_3$

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We have studied a quinary Fe-based superconductor Sr$_2$VFeAsO$_3$ by the measurements of x-ray diffraction, x-ray absorption, Mössbauer spectrum, resistivity, magnetization, and specific heat. This apparently undoped oxyarsenide is shown to be self-doped via electron transfer from the V$^{3+}$ ions. We observed successive magnetic transitions within the VO$_2$ layers: an antiferromagnetic transition at 150 K followed by a weak ferromagnetic transition at 55 K. The spin orderings within the VO$_2$ planes are discussed based on mixed valence of V$^{3+}$ and V$^{4+}$.

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I. INTRODUCTION

The discovery of high-temperature superconductivity (HTSC) in layered Fe-based compounds$^{1,2}$ represents an important breakthrough in the field of condensed-matter physics. So far, dozens of Fe-based superconductors in several crystallographic types have been discovered.$^2$ The common structural unit for the HTSC is Fe$_2$X$_2$ ($X$=As, Te, etc.) layers. The undoped Fe$_2$X$_2$ layers with formally divalent iron usually exhibit antiferromagnetic (AFM) spin-density-wave (SDW) instability.$^{3,4}$ HTSC emerges as the SDW ordering is suppressed by various kinds of doping$^{15-10}$ or applying pressures.$^{11}$ Both the magnetic ordering and superconductivity were suggested to be related to the nesting between the two cylinderlike Fermi surfaces near $\Gamma$ and M points.$^{12-16}$

Recently, superconductivity at 37 K was reported in a quinary oxyarsenide Sr$_2$VFeAsO$_3$ (hereafter called V21113),$^{17}$ consisting of perovskitelike Sr$_2$V$_2$O$_6$ and antifluorite-type Fe$_2$As$_2$ block layers. The observed superconductivity without extrinsic doping challenges the above paradigm, and immediately aroused several first-principles calculations.$^{18-22}$ However, the occurrence of superconductivity in the apparently undoped V21113 has not been clarified. Moreover, the calculated property of the Sr$_2$V$_2$O$_6$ blocks is very much scattered: including magnetic half-metallic,$^{18}$ nonmagnetic metallic,$^{19,20}$ and magnetic (Mott-type) insulating$^{22}$ states. Various kinds of possibilities on the magnetic ground state for V21113 were evaluated but no conclusive result was given.$^{21}$ Experimentally, few works$^{17,22}$ have been devoted to this system. It is simply not clear whether the Fe-site AFM order survives, let alone the magnetic property of the Sr$_2$V$_2$O$_6$ layers. The valence state of V, which is very crucial to understand the appearance of superconductivity, remains a puzzle. X-ray photoelectron spectroscopy (XPS) measurement suggested an "unexpected" V$^{5+}$ even in the oxygen-deficient V21113 samples, however, the result was then questioned because of the surface-sensitive nature for the XPS method.$^{23}$

In this paper, we report systematic experimental studies on the structure and physical properties of V21113. We employed x-ray absorption spectroscopy, capable of detecting the bulk properties, to examine the valence state of V. Our data unambiguous reveal mixed valence of V$^{3+}$ and V$^{4+}$, indicating that the Fe$_2$As$_2$ layers are actually self-doped due to the electron charge transfer from V to Fe. Our measurements have also identified two magnetic transitions at 55 K and 150 K, respectively, associated with the VO$_2$ layers. The observed weak ferromagnetism below 55 K and its coexistence with superconductivity at low temperatures make the V21113 system very unique in the family of Fe-based superconductors.

II. EXPERIMENTAL

Synthesis of single-phase 21113 samples turned out to be difficult$^{15}$ because of the tendency of nonstoichiometry$^{24}$ as well as the multi-interphase solid-state reactions. We have improved the sample quality by carefully controlling the stoichiometry. Samples of Sr$_2$V$_{1-x}$Mg$_x$FeAsO$_3$ ($x=0$ corresponds to undoped V21113 and $x=0.1$ refers to Mg-doped sample) were prepared using fine powders ($\sim$200 mesh, purity $\geq 99.9\%$) of SrO, MgO, V, Fe, Fe$_2$O$_3$, and As. The accurately weighed stoichiometric mixture was loaded in an alumina tube, preventing possible reactions with the quartz tube. The alumina tube, placed in a sealed quartz ampoule, was heated slowly to 1273 K, holding for 24 h. After the first time sintering, the sample was thoroughly ground, pressed into pellets, and sintered again in vacuum ($<10^{-4}$ Pa) at 1353 K for 48 h. All the operations of weighing, mixing, grinding, pelletizing, etc., were carried out in an argon-filled glove box with the water and oxygen contents less than 0.1 ppm.

Several measurements were performed as follows. Powder x-ray diffraction (XRD) was carried out using a D/Max-rA diffractometer with Cu Kα radiation and a graph-
spectra at different temperatures.

bration was performed with an
duced, indicating that the sample’s quality is significantly
employed Quantum Design PPMS-9
shaped samples using a standard four-terminal method. We
tive to the Fe foil. The resistivity was measured on bar-
ature. The reported isomer shift
surement system
were collected using a conventional constant acceleration
were measured in transmission
mode using powdered samples on beam lines U7B and U7C
were measured in transmission
As-Fe-As angle
transition can be ruled out in V21113. While the lattice
be seen. Thus, the SDW-ordering-related structural phase
FIG. 1. (Color online) (a) Rietveld refinement profiles for the
XRD data of Sr2V1−xMgxFexAsO3 [x=0 and 0.1 (inset)]. (b) Se-
lected XRD peaks at various temperatures. (c) 57Fe Mössbauer
spectra at different temperatures.

ite monochromator. The crystal structure at room tempera-
ture was refined by Rietveld analysis. The V K-edge x-ray
absorption spectra (XAS) were measured in transmission
mode using powdered samples on beam lines U7B and U7C
at the National Synchrotron Radiation Facility (NSRF),
Hefei, China. The water-cooled Si (111) plane bicrystal
monochromator was used. Calibration of spectrometer was
made using vanadium metal foil. The raw data were normal-
ized according to the previous literature.25 Mössbauer spectra
were collected using a conventional constant acceleration
drive. The sources were 50 mCi 57Co:Rh. The velocity cali-
bration was performed with an α-iron foil at room tempera-
ture. The reported isomer shift (IS) values for iron are re-
late to the Fe foil. The resistivity was measured on bar-
shaped samples using a standard four-terminal method. We
employed Quantum Design PPMS-9 (physical property mea-
surement system) and MPMS-5 (magnetic property measure-
system) to measure the specific heat and dc magnetiza-
tion, respectively.

III. RESULTS AND DISCUSSION

The XRD patterns are shown in Fig. 1(a). In comparison
with the previous report,17 the intensity of impurity peaks
(relative to that of the main peak) at 2θ~32° is greatly re-
duced, indicating that the sample’s quality is significantly
improved. According to the multiphase Rietveld refinement,26 the amount of impurity phases Sr2VO4 and
FeAs are less than 5%. The refined structural parameters for
Sr2V1−xMgxFexAsO3 (x=0 and 0.1) are listed in Table I. The
lattice constants of undoped V21113 are a little larger than
the reported values.17 The Mg substitution leads to a lattice
elongation. The As-Fe-As angle is very close to the ideal
value for a regular tetrahedron. On the other hand, the
V-02-V angle obviously deviates from 180°.

The low-temperature XRD experiments indicate no evi-
dence of structural phase transition in the whole tempera-
tures measured. Some of the data are shown in Fig. 1(b).
First, the (200) peak does not separate within the experimen-
tal limit, suggesting no usual tetragonal-to-orthorhombic
transition. Second, unlike the case in RFeAsO (R=La, Sm,
Gd, and Tb),27,28 no obvious splitting for the (220) peak can
be seen. Thus, the SDW-ordering-related structural phase
transition can be ruled out in V21113. While the lattice
parameters were found to decrease with decreasing tempera-
ture, the precise temperature dependence is expected to be
measured by a future XRD study with synchrotron radia-
tions.

The Mössbauer spectra [Fig. 1(c)] show a quadrupole
doublet at all the temperatures, in contrast with the sextet
line for the AFM SDW ordered state.27,29 From the data we
deduced no effective paramagnetic moment, therefore, the
iron does not carry magnetic moment on its own. Accord-
ingly no magnetic ordering at the Fe sublattice is expected.
The IS value is similar to those observed for other ferroar-
sene systems,29 suggesting that the iron is basically divalent.

Figure 2 shows the V K-edge XAS for V21113 and its
reference vanadium oxides. It has been well established that,
in a number of V compounds, the position of the character-

TABLE I. Crystallographic data of Sr2V1−xMgxFexAsO3 (x=0 and
0.1) at room temperature. The space group is P4/nmm. The
atomic coordinates are as follows: Sr1 (0.25, 0.25, z); Sr2 (0.25,
0.25, z); V (0.25, 0.25, z); Fe (0.25, 0.75, 0); As (0.25, 0.25, z);
O1 (0.25, 0.25, z); and O2 (0.25, 0.75, z). BVS refers to bond valence
sum (Ref. 30), reflecting the formal valence of an ion investigated.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>x=0</th>
<th>x=0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>3.9352(1)</td>
<td>3.9334(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15.6823(5)</td>
<td>15.7488(7)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>242.86(1)</td>
<td>243.66(2)</td>
</tr>
<tr>
<td>Rwp</td>
<td>8.59</td>
<td>8.82</td>
</tr>
<tr>
<td>S</td>
<td>1.68</td>
<td>1.70</td>
</tr>
<tr>
<td>z of Sr1</td>
<td>0.8090(1)</td>
<td>0.8091(1)</td>
</tr>
<tr>
<td>z of Sr2</td>
<td>0.5857(1)</td>
<td>0.5865(1)</td>
</tr>
<tr>
<td>z of V</td>
<td>0.3080(2)</td>
<td>0.3074(2)</td>
</tr>
<tr>
<td>z of As</td>
<td>0.0893(1)</td>
<td>0.0880(2)</td>
</tr>
<tr>
<td>z of O1</td>
<td>0.4248(4)</td>
<td>0.4257(5)</td>
</tr>
<tr>
<td>z of O2</td>
<td>0.2934(3)</td>
<td>0.2952(4)</td>
</tr>
<tr>
<td>BVSV for VIII</td>
<td>2.95</td>
<td>N.V.</td>
</tr>
<tr>
<td>BVSV for IV</td>
<td>3.29</td>
<td>N.V.</td>
</tr>
<tr>
<td>BVSV for V</td>
<td>3.46</td>
<td>N.V.</td>
</tr>
<tr>
<td>V-02-V angle (deg)</td>
<td>166.7(2)</td>
<td>168.8(2)</td>
</tr>
<tr>
<td>As-Fe-As angle (deg)</td>
<td>109.1(1)</td>
<td>109.7(1)</td>
</tr>
</tbody>
</table>
FIG. 2. (Color online) Vanadium K-edge x-ray absorption spectra for Sr₂VFeAsO₃ as well as some reference compounds V₂O₃, VO₂, and V₂O₅. The insets show the determination of the valence of V (Vₐ) by the absorption threshold, Eₜₜₜₜₜ.

Phonic absorptions (such as absorption threshold, pre-edge peak, and main absorption edge) vary linearly with the valence of V (Vₐ). The main edge of V21113 lies in between those of V₂O₃ and VO₂, clearly indicating the mixed valence state for V. The pre-edge structure (to the left of the main edge) of V21113 resembles that of V₂O₃, suggesting that V3⁺ is dominant. One can fit the pre-edge of V21113 by the addition of weighed XAS of V₂O₃ and VO₂. The best fitting gives Vₐ=3.22. In fact, Vₐ can be better determined by using the characteristic absorption threshold (Eₜₜₜₜₜ). As shown in the insets of Fig. 2, Eₜₜₜₜₜ increases steadily on going along V₂O₃→VO₂→V₂O₅. Assuming a linear relation of Eₜₜₜₜₜ vs Vₐ, we obtain Vₐ=3.18±0.05, consistent with the former estimation. Here we note that the structural parameters of V21113 also support the conclusion about the V valence. The calculated bond-valence-sum values for V in Table I verify the dominant V3⁺ with minority of V4⁺ in V21113.

Because of the overall charge neutrality, the mixed valence of V immediately suggests that the Fe₂As₂ layers are “self” (or internally) electron doped by the charge transfer from the V3⁺ ions (conversely, the Sr₅V₂O₈ layers are self-hole-doped). This conclusion is consistent with the measurements of Hall and Seebeck coefficients, which show electron-dominant transport behavior (not shown here), and also with the band calculations which indicate the occupation number of 3d electrons per V being less than 2. The absence of Fe-site AFM ordering and appearance of SC transition (see below) are thus naturally understood within the established paradigm for Fe-based HTSC.

In Fig. 3, we plot the temperature dependence of resistivity (ρ), magnetic susceptibility (χ), and specific heat (C) for V21113 along with Sr₂V₀.₅M₀.₅FeAsO₃ as a reference. The V21113 sample shows SC transition at 24 K, which is somewhat lower than previously reported. The lowered Tc is mainly ascribed to the “overdoped” state since the self-doping level achieves ~18% (from the obtained Vₐ above). As we see, the Mg-doped sample shows an enhanced Tc of 30 K. This result does suggest that the undoped V21113 is overdoped, because the Mg-for-V substitution induces holes, which partially compensates the heavy electron doping. Another reason for the lowered Tc could be due to the V-for-Fe antisite occupation, as suggested by a very recent report.

For V21113, an anomaly at T₁=150 K is clearly shown in the derivative of ρ(T) as well as χ(T) and C(T) curves. In particular, the anomaly in C(T) points to an intrinsic second-order phase transition since specific heat measures bulk properties (note that the amount of impurities is less than 5%). For the Mg-doped sample, however, such an anomaly is completely suppressed. Since the Fe-site magnetic ordering was ruled out by the above Mössbauer study, we conclude that the 150 K transition V21113 is intrinsic and directly related to the V atoms.

The χ(T) data in the range of 300>T>150 K obey the Curie-Weiss law, χ=χ₀+C_Curie/(T−θₜₜₑ), where C_Curie denotes the Curie constant and θₜₑ the Weiss temperature. Since the Fe atoms have no effective paramagnetic moments, as revealed by the above Mössbauer study, we can estimate the effective magnetic moments of V, which gives P_eff=1.2 μB/V by the data fitting. The significantly lowered P_eff (compared with the spin-only value for either V³⁺ or V⁴⁺) could be due to the d-p hybridization in connection with the mixed valence. The fitted θₜₑ value is 52 K, implying dominant ferromagnetic (FM) correlations between the magnetic moments. By subtracting C(T) of Mg-doped V21113 from that of the undoped V21113, the magnetic entropy for the transition is calculated to be ~1.1 J mol⁻¹ K⁻¹, which is much lower than the expected value of R ln(2S+1) (S=1 for V³⁺ and S=1/2 for V⁴⁺). The result suggests that short-range magnetic order is established at the temperatures far above...
150 K. Note that the steplike increase in $\chi$ at the transition does not mean a FM transition because the $M(H)$ curve for $70 < T < 150$ K is linear [see Fig. 4(c)]. In fact, the AFM ordering of A or C type possibly exhibits an increase in $\chi$ at the magnetic transition.$^{32}$

In addition to the 150 K transition, another anomaly at $T_2 \sim 55$ K can be clearly seen in $1/(\chi - \chi_0)$, as shown in Fig. 3(b). Specific-heat data also show a small anomaly around 55 K. However, the Mg-doped sample, which contains a little more impurities, simultaneously loses the two anomalies. This fact strongly suggests that the 55 K anomaly is also intrinsic and related to the Sr$_2$V$_2$O$_6$ layers. Figure 4 supplies more information about this second transition. At low fields, the magnetization diverges at 55 K for field-cooling (FC) and zero FC (ZFC) modes, suggesting a ferromagnetic transition. The FM state is further supported by the $M(H)$ curve, where a magnetic hysteresis loop is clearly observed. The very small extrapolated residual magnetization ($M_h \sim 10^{-3}$ $\mu_B$/V at 35 K) and lack of saturation in $M$ at high fields indicate that it is actually a weak FM (WFM). The WFM nature is consistent with the above Mössbauer spectra which show negligibly small transferred hyperfine field (below 0.07 T) at the Fe site for $T=20$ and 40 K. Nevertheless, the SC magnetic loop [Fig. 4(d)] exhibits obvious asymmetry relative to the horizontal axis, suggesting significant contributions of WFM in the SC state. It is noted that the coexistence of SC and WFM differs with the previous finding of the coexistence of SC and strong ferromagnetism (due to 4\$ local moments) in EuFe$_2$(As$_{0.2}$P$_{0.3}$)$_2$.10

Now, let us discuss the possible origin of the two magnetic transitions within the Sr$_2$V$_2$O$_6$ layers. The electronic configurations of V$^{3+}$ and V$^{4+}$ are $d^2$ and $d^3$, respectively. Within an ionic model, the lowest V 3 orbital degenerate $d_{xz}$ and $d_{yz}$ due to the crystal-field splitting. In the case of pure V$^{3+}$, the electron occupation is $d_{xz}^\uparrow d_{yz}^\uparrow$, according to the Hund’s rule. The ground state of the square lattice of V in the VO$_2$ planes is AFM due to superexchange interaction.$^{32}$ In V21113, there are $\sim 18\%$ V$^{4+}$ ions and the Zener’s double exchange favors ferromagnetic spin arrangement in the same VO$_2$ plane for the gain of kinetic energy. This could result in an in-plane FM state. However, the electron hopping integrals in VO$_2$ planes are direction dependent. The amplitude of the hopping integral of $d_{xz}$ along y axis (or $d_{yz}$ along x axis), $t'$, is much smaller than that of $d_{yz}$ along x axis (or $d_{xz}$ along y axis), $t$. This leads to another possible spin array in the VO$_2$ planes, i.e., a C-type AFM state where the spins are parallel along x axis and antiparallel along y axis, or vice versa. By a simplified mean-field analysis, we estimate that the FM state is more stable if $|t'|/J > 2(1-\delta)/\delta$, with $J$ the neighboring spin coupling and $\delta$ the concentration of V$^{4+}$.

The scenario of in-plane FM state coincides with the aforementioned positive Weiss temperature. Thus the observed transition at $T_2 = 55$ K may be ascribed to an A-type AFM ordering with AFM coupling along the c axis. The WFM transition at $T_2 = 55$ K may be interpreted as the spin canting within the framework of double exchange proposed by de Gennes,$^{33}$ although usually one would expect a more substantial magnetic moment. As for the scenario of in-plane C-type AFM, the WFM transition is still an open question. One possibility is due to the nonzero Dzyaloshinsky-Moriya interaction, which plays an important role for the intriguing magnetic responses in other vanadium oxides.$^{34}$

**IV. CONCLUDING REMARKS**

To summarize, we have demonstrated experimentally that superconductivity in undoped Sr$_2$VFeAsO$_3$ is induced by a self-doping mechanism, i.e., an interlayer charge transfer from V to Fe. Neither structural phase transition nor Fe-site SDW ordering was observed, consistent with the electron-doped state in the Fe$_2$As$_2$ layers. In addition, we have identified two intrinsic magnetic transitions in connection with the mixed valence of V. The transition at 150 K is ascribed as an AFM ordering. The following transition at 55 K is weakly ferromagnetic, probably due to a spin canting process. The WFM transition renders a rare example of coexistence of SC
and WFM, which will be of great interest for the future studies. Further experiments such as neutron diffractions are desirable to check the spin structure of V and to confirm that the moment does not come from Fe.

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