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Transition of stoichiometric Sr_2VO_3FeAs to a superconducting state at 37.2 K

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The superconductor $Sr_4V_2O_6Fe_2As_2$ with transition temperature at 37.2 K was successfully fabricated. It has a layered structure with the space group of $p4/nmm$ and with the lattice constants $a=3.9296$ Å and $c=15.6732$ Å. The observed large diamagnetization signal and zero resistance demonstrated the bulk superconductivity. The broadening of resistive transition was measured under different magnetic fields revealing a rather high upper critical field. The results also suggest a large vortex liquid region that reflects high anisotropy of the system. The Hall-effect measurements revealed dominantly electronlike charge carriers in this material. The superconductivity in the present system may be induced by oxygen deficiency or the multiple valence states of vanadium.

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Since the discovery of superconductivity[1] at 26 K in oxyarsenide $LaFeAsO_{1-x}F_x$, tremendous attention has been paid to searching new superconductors in this family. Among the superconductors with several different structures,[2–6] the highest T_c has been raised to 55–56 K (Refs. 7–11) in doped oxy-iron-arsenides (F-doped LnFeAsO, the so-called 1111 phase, and Ln=rare-earth elements) or the fluoride derivative iron-arsenides (Ln-doped AEFeAsF, AE=alkaline-earth elements).[12] The superconductivity can also be induced by applying high pressure to the undoped parent samples.[13,14] Although it remains unclear what governs the mechanism of superconductivity in the FeAs-based system, it turns out to be clear that the parent phases in many families are accompanied by an antiferromagnetic (AF) order and the superconductivity can be induced by suppressing this magnetic order. A typical example was illustrated in the $(Ba,Sr)Fe_2As_2$ (so-called 122) system: the AF order is suppressed and superconductivity was induced by either doping K to the Ba or Sr sites[2,15,16] or doping Co to the Fe sites.[17,18] On the other hand, superconductivity was also found in the parent phase of FeP-based system, such as LaFePO ($T_c=2.75$ K),[19] or in LiFeAs.[3,4] Very recently superconductivity at about 17 K was found in another FeP-based parent compound $Sr_4Sc_2O_6Fe_2P_2$ (so-called 42622).[20] Due to the absence of the AF order in the superconductors mentioned above, one naturally questions whether the AF order is a prerequisite for the superconductivity in the iron-pnictide system. As far as we know, no superconductivity was detected in the undoped (thus called as the parent) phase of some FeAs-based compounds, including the 1111, 122, and the recently discovered 42622 and 32522 phases.[21–25] Although some trace of superconductivity was reported in the doped FeAs-based 42622 or 32522 compounds, the high-T_c superconductivity was not supported by a clear large diamagnetization signal.[22,23] In this Rapid Communication, we report the discovery of superconductivity at 37.2 K in the new compound $Sr_4V_2O_6Fe_2As_2$. This work presents the unambiguous evidence for high-temperature superconductivity in the FeAs-based 42622 system.

The polycrystalline samples were synthesized by using a two-step solid-state reaction method.[26] First, SrAs powders were obtained by the chemical reaction method with Sr pieces and As grains. Then they were mixed with V_2O_5 (purity 99.9%), SrO (purity 99%), Fe and Sr powders (purity 99.9%), in the formula $Sr_4V_2O_6Fe_2As_2$, ground and pressed into a pellet shape. The weighing, mixing, and pressing processes were performed in a glove box with a protective argon atmosphere (the H_2O and O_2 contents were both below 0.1 ppm). The pellets were sealed in a silica tube with 0.2 bar of Ar gas and followed by a heat treatment at 1150 °C for 40 h. Then it was cooled down slowly to room temperature. The x-ray diffraction (XRD) patterns of our samples were carried out by a *Mac-Science* MXP18A-HF equipment with $\theta-2\theta$ scan. The XRD data taken using powder sample were analyzed by the Rietveld fitting method using the GSAS suite.[27] The dc susceptibility of the samples were measured on a superconducting quantum interference device (Quantum design, magnetic property measurement system 7 T). The resistivity and Hall-effect measurements were done using a six-probe technique on the Quantum design instrument physical property measurement system with magnetic fields up to 9 T. The temperature stabilization was better than 0.1%, and the resolution of the voltmeter was better than 10 nV.

The XRD pattern for the sample $Sr_4V_2O_6Fe_2As_2$ is shown in Fig. 1. This compound consists of a stacking of antifluorite Fe_2As_2 layers and perovskite-type $Sr_4V_2O_6$ layers. Rietveld refinement shown by the solid line in Fig. 1 gives good agreement between the data and the calculated profiles. The impurity phase was detected and found to come mainly from Sr_2VO_4. The calculated XRD pattern (solid line) of the mixture was obtained by adopting a ratio of $Sr_4V_2O_6Fe_2As_2:Sr_2VO_4=13:1$. Lattice parameters for the tetragonal unit cell were determined to be $a=3.9296$ Å and $c=15.6732$ Å. In Table I, the structure parameters were listed with agreement factors: $wR_p=13.23\%$, and $R_p=9.35\%$.

To confirm the presence of bulk superconductivity in our sample, we measured the magnetization of our sample using the dc susceptibility method. In Fig. 2(a) we present the temperature-dependent dc susceptibility data measured with a dc field of 10 Oe. The data were obtained using the zero-field-cooling and field-cooling modes. The onset supercon-

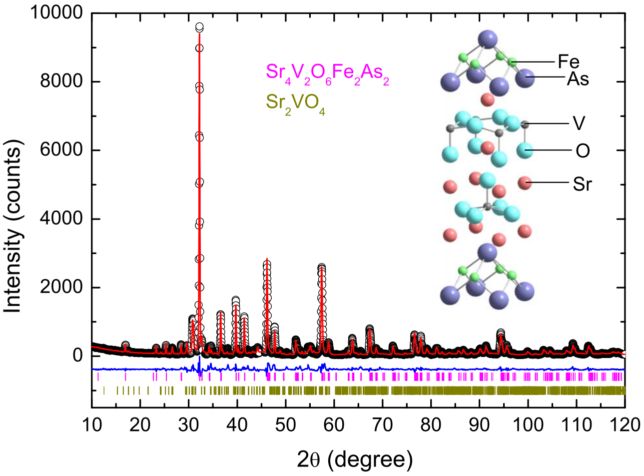

FIG. 1. (Color online) x-ray diffraction patterns for the sample $Sr_4V_2O_6Fe_2As_2$. Bottom: Sr_2VO_4 was included in the refinement as the minor impurity phase.

ducting transition temperature as determined from the dc magnetization is about 31.5 K. In Fig. 2(b), we show the temperature dependence of resistivity under zero field in the temperature region of up to 300 K. A clear superconducting transition can be observed in the low-temperature region. The onset critical transition temperature was determined to be about 37.2 K from this curve, and the resistivity drops to zero at the temperature of about 31 K, being rather consistent with the onset transition point in the dc susceptibility curve and further confirming the bulk superconductivity in this compound. A metallic behavior can be seen above the transition temperature. Interestingly the resistivity in the normal state exhibits a plateaulike shape in the high-temperature region. This could be attributed to the incomplete suppression to the possible AF order (if it exists for this compound), or it is similar to that in the hole doped FeAs superconductors $Ba_{1-x}K_xFe_2As_2$ (Ref. 2) and $(La,Pr)_{1-x}Sr_xFeAsO$,[28,29] where a general feature of bending down of resistivity was observed in the high-temperature region. If the former case is true, the superconducting transition temperature can be further increased by adding electrons or holes into the sample.

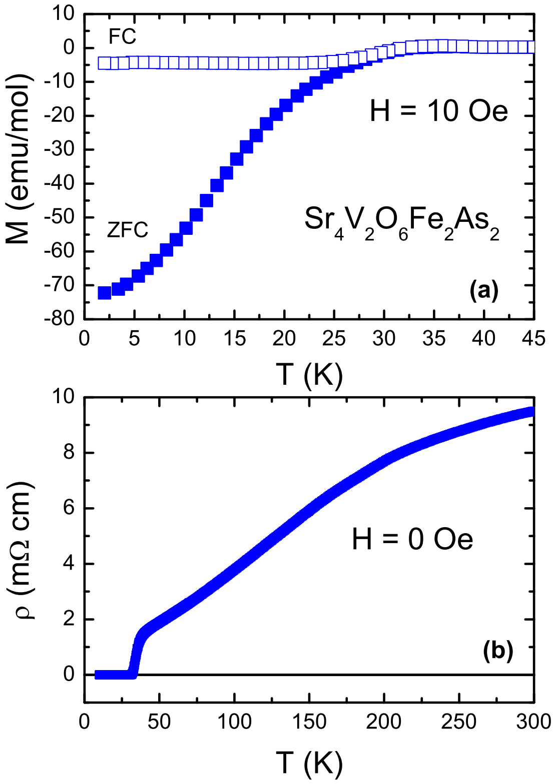

FIG. 2. (Color online) (a) Temperature dependence of the dc susceptibility for the sample $Sr_4V_2O_6Fe_2As_2$. The dc susceptibility data were obtained using the zero-field-cooling and field-cooling modes with a dc magnetic field of 10 Oe. The onset superconducting transition temperature was determined to be 31.5 K. (b) Temperature dependence of the resistivity under zero field in temperature region up to 300 K.

TABLE I. Fitting parameters for $Sr_4V_2O_6Fe_2As_2$. $wR_p = 13.23\%$ and $R_p = 9.35\%$.

Atom	Site	*x*	*y*	*z*
V	2*c*	0.2500	0.2500	0.3081
Fe	2*a*	0.2500	0.7500	0.0000
Sr	2*c*	0.7500	0.7500	0.1903
Sr	2*c*	0.7500	0.7500	0.4145
As	2*c*	0.2500	0.2500	0.0909
O	4*f*	0.2500	0.7500	0.2922
O	2*c*	0.2500	0.2500	0.4318

We present the resistivity data in low-temperature region under different fields in Fig. 3(a). The transition curve is clearly rounded near the onset transition temperature, showing the possibility of the presence of superconducting fluctuation in this system. This is actually understandable since the system now becomes more two-dimensional like due to the very large spacing distance between the FeAs planes. One can see that the onset transition temperature moves very little at a field as high as 9 T. The zero-resistance temperature moves to low temperatures rapidly, showing a broadening effect induced by the magnetic field that may imply the presence of superconducting weak link between the grains in the present sample. We have pointed out that the evolution of onset transition temperature with field mainly reflects the information of upper critical field along the *ab* plane for a polycrystalline sample.[26] Therefore we took a criterion of 90% ρ_n to determine the onset critical temperatures under different fields. Surprisingly, we got a rather large slope of $H_{c2}(T)$ near T_c, $(dH_{c2}/dT)_{T=T_c} \approx -11.3$ T/K. This value is obviously larger than that obtained in some FeAs-based superconductors[26,29] but is close to $dH_{c2}^{ab}/dT = -9.35$ T/K in $Ba_{0.6}K_{0.4}Fe_2As_2$ (Ref. 30) and consequently results in a rather high upper critical field of about 302 T using the Werthamer-Helfand-Hohenberg (WHH) formula $H_{c2}(0) = -0.69T_c dH_{c2}/(dT)_{T=T_c}$.[31] In Fig. 3 we present also the irreversibility line H_{irr} taking with the criterion of 0.1% ρ_n. It is found that a large region exists between the upper critical field $H_{c2}(T)$ and the irreversibility field $H_{irr}(T)$. As mentioned before, this large separation may be induced by the

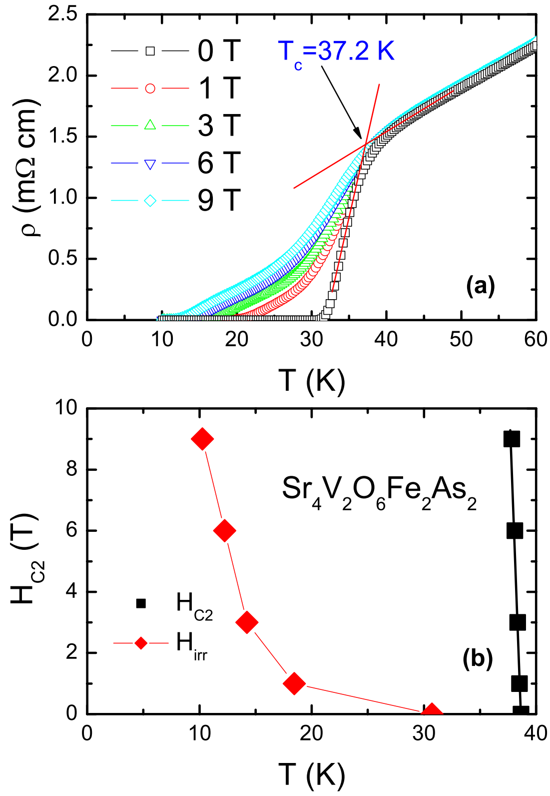

FIG. 3. (Color online) (a) Temperature dependence of resistivity in the low-temperature region under different fields. The onset transition temperature was determined to be 37.2 K in the data under zero field. (b) The phase diagram plotted as H_{c2} versus T. A criterion of 90% ρ_n was taken to determine the upper critical fields. The irreversibility line H_{irr} taking with the criterion of 0.1% ρ_n is also presented in this figure.

weak-link effect between the grains. In this sense the superconducting coherence length (most probably along the c axis) is shorter in this material than in other families, such as 1111 and 122. Furthermore, this large gap between $H_{c2}(T)$ and $H_{irr}(T)$ can also be explained by the stronger thermal fluctuation effect of vortices in the present system due to the higher anisotropy.

In order to know the electronic properties of this parent phase, we measured the Hall effect in the normal state. Figure 4 shows the temperature dependence of the Hall coefficient $R_H(T)$. As shown in the inset, the raw data of the transverse resistivity ρ_{xy} are negative and exhibit a linear relation with the magnetic field. This is similar to that in other FeAs-based superconductors.[26] The Hall coefficient R_H is negative in the measured temperature region indicating that the electronlike charge carriers are dominating the conduction. However, as in all other FeAs-based superconductors, $R_H(T)$ shows a strong temperature dependence, which is actually anticipated by the multiband picture: the electron scattering rate $1/\tau_i$ of each band will vary with temperature in a different way; therefore, a combined contribution of multiple bands will lead to strong temperature dependence of Hall coefficient.[32]

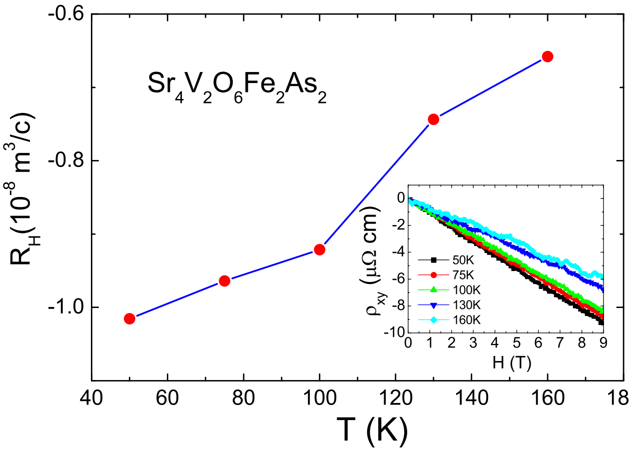

FIG. 4. (Color online) Temperature dependence of Hall coefficient $R_H(T)$ determined at 9 T from the transverse resistivity ρ_{xy} shown in the inset. It is clear that the transverse resistivity ρ_{xy} is negative and linearly related to the magnetic field, suggesting that the electron conduction is dominated by the electronlike charge carriers in $Sr_4V_2O_6Fe_2As_2$.

As stated previously, without additional doping, namely, in the stoichiometric (thus called as "parent" phase) of FeP-based materials[19,20] and LiFeAs,[3,4] superconductivity shows up but with relatively low T_c. So far there has been no report about the existence of the static long range AF order in the parent or doped phase of FeP-based compound and in LiFeAs. In the FeAs-based parent phase, however, in most cases [with an exception of LiFeAs (Refs. 3 and 4) and FeAs-32522 parent phase][21] an AF order was observed in the low-temperature region and the superconductivity can only be achieved by suppressing this unique AF order. Recently through careful Hall-effect measurements and analysis, it was concluded that the AF order and superconductivity actually compete with each other for the quasiparticle density of states in the underdoped $Ba(Fe_{1-x}Co_x)_2As_2$.[33] In the present work the superconductivity was observed in the undoped phase of $Sr_4V_2O_6Fe_2As_2$, and this raises the question again whether the AF order is a prerequisite for the superconductivity. One possibility for explaining the superconductivity in this system is that the oxygen content in the sample may be tunable since there are many occupying sites for oxygen atoms in the structure. Oxygen deficiency in the system implies a doping of electrons and thus leads to the superconductivity. If this is true, doping to this "parent" phase will lead to the suppression of superconductivity and make the AF order emerge. Another possibility may be due to the multiple valence states of vanadium. For example, in the compound V_2O_3, the vanadium has a "3+" valence state, while that in Sr_2VO_4 is "4+." Therefore our compound here provides another platform for the doping and tuning of the superconductivity and AF magnetism. In addition, there may be other possibilities to explain the superconductivity in this system. For example, the present system shares the similarity of the FeP-based and LiFeAs "parent" compounds in which no evidence of AF order was found. Our results will call for band structural calculations for the detailed structure of the Fermi surface for this new compound. A naive understanding would assume that the FeAs planes are very similar to that in other systems; thus, it has no reason for the absence of the

AF order in the present system if it is induced by the nesting effect. Since this is the first observation of superconductivity (with a relatively high transition temperature) in 42622 phase of the FeAs-based compound, our discovery will stimulate the in-depth understanding to the mechanism of superconductivity in the iron-pnictide superconductors.

In summary, superconductivity with $T_c=37.2$ K was found in the FeAs-based compound $Sr_4V_2O_6Fe_2As_2$. The x-ray diffraction measurement showed that this compound has a layered structure with the space group of $P4/nmm$. Both the large diamagnetization signal and zero resistance were detected, indicating an unambiguous evidence for bulk superconductivity. The broadening of resistive transition was measured under different magnetic fields, and the upper critical field (most possibly the H_{c2}^{ab}) determined by using the WHH formula is rather high. The Hall-effect measurements showed that the conduction in this material was dominated by the electronlike charge carriers. Beside the stoichiometric LiFeAs, this is another study of superconductivity in the stoichiometric phase of the FeAs-based compound at ambient pressure. Based on this material platform, more new superconductors, with probably higher T_c, are expected.

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