

Studies on the superconductivity for the “111” type iron arsenide superconductor

Xian-cheng WANG (望贤成), Qing-qing LIU (刘青青), Liu-xiang YANG (杨留响),
Zheng DENG (邓正), Yu-xi LÜ (吕玉玺), Wei-bo GAO (高伟波), Si-jia ZHANG (张思佳),
Ri-cheng YU (禹日成), Chang-qing JIN (靳常青)✉

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100080, China
E-mail: jin@aphy.iphy.ac.cn

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The “111” type Li_xFeAs (x ranges from 0.8 to 1.2) with Cu_2Sb type tetragonal structure was synthesized with T_c 18 K. The isostructure NaFeAs was further studied, which shows superconductivity with T_c up to 26 K. The effect of pressure on superconductivity was investigated.

Keywords iron arsenide superconductor, LiFeAs

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1 Introduction

Since the discovery of superconducting LaFeAsO with T_c 26 K [1], great interest has been stimulated in exploring new superconductors and studying the novel superconducting mechanism in the iron arsenide system [1–8]. Up to now, the critical temperature for iron arsenide superconductors has been raised to ~ 50 K, which is the highest for noncuprate superconductors. Three types of iron arsenide superconductors have been found so far: (1) “1111” type RFeAsO [1–6] (R =rare-earth metal), (2) “122” type AeFe_2As_2 (Ae =alkaline-earth metal) [7], (3) “111” type AFeAs (A =Li, Na) [8].

Similar to cuprate superconductors in which $[\text{CuO}_2]$ layers play a key role for superconducting, these iron based superconductors have $[\text{FeAs}]$ layers that serve as a carrier conduction path. The part sandwiched between $[\text{FeAs}]$ layers is the charge reservoir providing carriers. Both parent compounds for “1111” and “122” exhibit spin-density-wave (SDW) anomaly and magnetic order with decreasing temperature [1–7]. Upon doping these parent compounds or applying high pressure the SDW anomaly can be suppressed resulting in the appearance of superconductivity. It is considered that superconductivity competes with SDW in these systems and the Cooper pairing is somehow related with spin fluctuation.

In this paper we report the detail of sample synthesis as well as the property characterizations of “111”

type AFeAs superconducting family (A represents alkaline metal Li or Na).

2 Experimental

The polycrystalline samples of nominal composition A_xFeAs (x ranges from 0.8 to 1.2) were synthesized by solid state reaction method using Li or Na, FeAs as starting material. The FeAs precursors were synthesized from high purity Fe and As powders that were sealed into an evacuated quartz tube and sintered at 800°C for 60 h. The obtained FeAs powder was pressed into pellets. Then the pellets and Li or Na pieces were put into an alumina crucible according to the nominal formula A_xFeAs and finally sealed in quartz tubes. They were then sintered at 900°C for LiFeAs or at 800°C for NaFeAs for 30 h. The reaction products were pressed into pellets after grinding. The pellet wrapped with Ta foil was sealed in a quartz tube under Ar. The sample was annealed at 800°C for 30 h again. All preparative manipulations were carried out in a glove box protected with high purity Ar.

The obtained samples were characterized by X-ray powder diffraction with a Mac Science diffractometer. The magnetic properties of the samples were measured using a superconducting quantum interference device (SQUID). The electric conductivity was measured using the standard four probe method.

3 Results and discussion

The “111” type AFeAs compounds crystallized into Cu_2Sb type tetragonal layered structure with space group P4/nmm , which is shown in Fig. 1(a) [9]. The obtained Li_xFeAs samples were hygroscopic. The X-ray diffraction pattern for these samples with nominal composition Li_xFeAs is shown in Fig. 2. The lattice parameters for LiFeAs samples at room temperature are $a = 3.771(5) \text{ \AA}$ and $c = 6.357(4) \text{ \AA}$. The angles of As–Fe–As have two values termed α (102°) and β (112°) respectively for LiFeAs . The bond length for Fe–As and adjacent iron distance is 2.4 \AA and 2.6 \AA respectively [8]. It shows that the tetrahedron of FeAs_4 is chemically compressed due to the small ion radius Li atoms interlaced into $[\text{FeAs}]$ layers. For comparison, Fig. 1 (b), (c) also displays the structure figures for “1111” and “122” type compounds. All the three types of superconductors resemble each other in that they all contain the $[\text{FeAs}]$ layer. What is more, LiFeAs is an interesting model compound to study the unconventional superconducting mechanism for iron arsenide superconductors since it crystallizes into a simple crystal structure that makes

LiFeAs more like an “infinite layer structure” compared with the prototype ACuO_2 for high T_c cuprate.

Figure 3 shows the dc magnetic susceptibility for the sample with nominal composition $\text{Li}_{1.0}\text{FeAs}$ measured in both zero field cooling (ZFC) & field cooling (FC) mode with a $H = 30 \text{ Oe}$. The large Meissner signal ($> 10\%$) indicates the bulk superconducting nature of the sample. The inset shows the dc magnetic susceptibility of samples for $x = 0.8, 1.2$. The superconducting transition temperature T_c values for all the samples range from 16 K to 18 K. It seems that T_c for Li_xFeAs sample is not sensitive to the nominal doping.

The temperature dependence of the electric conductivity of samples with nominal composition $\text{Li}_{1.0}\text{FeAs}$ is shown in Fig. 4. The parent LiFeAs shows metallic behavior with a pronounced curvature at a wide temperature range below room temperature. It could be the intrinsic property of LiFeAs or it may result from the inhomogeneous composition that leads to a little Li instoichiometry in LiFeAs compounds. It is worth mentioning that there is no electric conductivity anomaly in the ρ – T curve that usually results from the SDW-related phase transition.

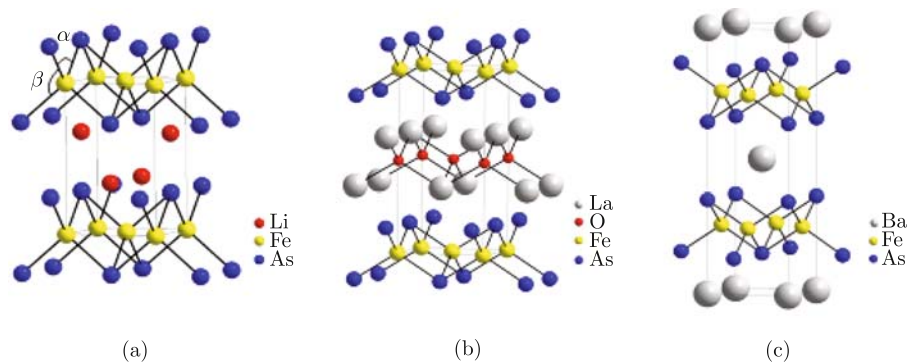


Fig. 1 Crystal structure of (a) “111” LiFeAs , (b) “1111” LaFeAsO , (c) “122” BaFe_2As_2 .

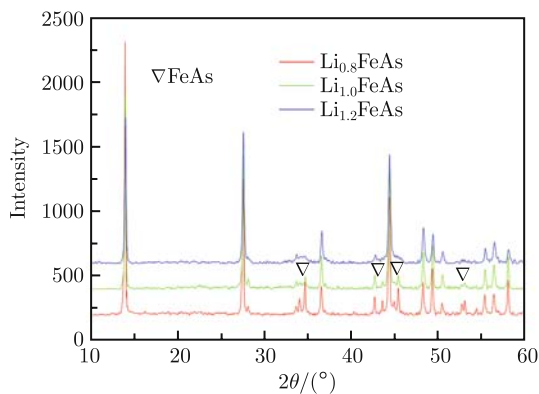


Fig. 2 The X-ray diffraction pattern of samples with nominal composition Li_xFeAs (x ranges from 0.8 to 1.2).

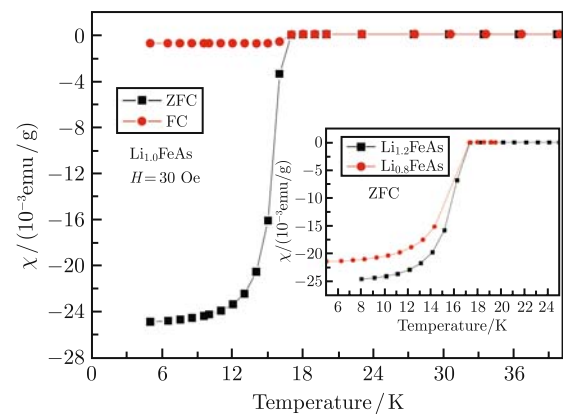


Fig. 3 The dc magnetic susceptibility for sample with nominal composition $\text{Li}_{1.0}\text{FeAs}$ measured in both zero field cooling (ZFC) & field cooling (FC) mode with a $H = 30 \text{ Oe}$. The inset shows the dc magnetic susceptibility of Li_xFeAs samples ($x=0.8, 1.2$).

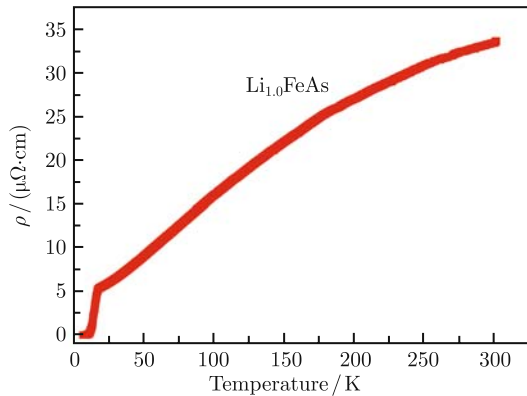


Fig. 4 The temperature dependence of the electric conductivity of samples with nominal composition $\text{Li}_{1.0}\text{FeAs}$.

For LaFeAsO and BaFe_2As_2 compounds, the electric conductivity sharply drops at ~ 150 K and ~ 140 K respectively, which provides the evidence of SDW existing in these systems [1, 7]. At lower temperature these parent iron arsenide compounds have C-type antiferromagnetic structures [10–12]. When they are doped or applied pressure, the antiferromagnetic-SDW is suppressed gradually resulting in the appearance of superconductivity. SDW seems to be associated with superconductivity in these iron arsenide compounds. However, this SDW related anomaly characterized by the sharp drop of resistance seems absent for LiFeAs as shown in Fig. 4. The LDA calculated results for “111” LiFeAs show that it has similar band dispersions as well as the shape of the Fe-3d density of states at Fermi level to those for “1111” type LaOFeAs or “122” type BaFe_2As_2 system [13, 14]. It also suggested that the ground state for LiFeAs should be antiferromagnetic structure [14]. To understand the magnetic ordering of “111” type LiFeAs is a very interesting topic for either theoretical or experimental studies.

A possible reason for the absence of SDW in LiFeAs system is that the chemical in stoichiometry at Li site leads to the suppression of magnetic ordering. Juza and Langer have suggested that Li-rich is required for LiFeAs synthesis [9]. An alternative reason is that the absence of SDW is the intrinsic property of LiFeAs . Superconductivity could be induced in the parent compounds of “122” type iron arsenide by pressure and both the structural and magnetic transitions associated with SDW were suppressed gradually when pressure was applied on them [15–17]. Compared to these “122” parent compounds, LiFeAs has a significant compression structure for the smaller Li ion interlaced into $[\text{FeAs}]$ layers. Therefore, it can be considered that LiFeAs compound has been applied with chemical inner pressure, which induces the suppression of SDW. In another point of view, the absence of SDW in LiFeAs system might result from its special lattice parameters. In the $[\text{FeAs}]$ layer, there are two types of electron correlation interactions. The

super-exchange interaction between adjacent Fe atoms mediated by As atom tends to form antiferromagnetic order; while the direct exchange interaction between adjacent Fe atoms tends to form ferromagnetic order. As we know, the distance of the adjacent Fe atoms in LiFeAs crystal is the smallest and the bond length of Fe-As is the longest among the iron arsenide compounds, which might increase the ferromagnetic coupling and weaken the antiferromagnetic coupling respectively. First-principles electronic calculations show that the energy difference between the antiferromagnetic and ferromagnetic state in LiFeAs system is only 0.03 eV per formula unit [18]. This very small energy difference raises the possibility of mixed electronic states at ambient temperature. So the unique small lattice parameters of LiFeAs might make SDW absent in this system.

The ρ - T curve at different pressures for the sample of $\text{Li}_{1.0}\text{FeAs}$ has been measured also. The pressure dependence of the T_c curve is shown in Fig. 5. T_c value decreases linearly with increasing pressure and the slope dT_c/dP is -1.38 K/GPa. When $\text{LaFeAsO}_{1-x}\text{F}_x$ was compressed with the external pressure, the T_c was raised from 26 K to 43 K [19]. To study the effect of pressure on superconducting transition temperature, many experiments studying the crystal structure evolution under high pressure for iron based superconductors have been carried out [18, 20–21]. When pressure is applied to LiFeAs sample, the value of α related to As-Fe-As bond angle shown in Fig.1 decreases and β increases [21], which make the tetrahedron of FeAs_4 further depart from a regular one. Because the density state at the Fermi level in iron arsenide is sensitive to the As-Fe-As angular, there is a strong correlation between the shape of FeAs_4 tetrahedra and T_c . In the “1111” type compounds T_c would reach the maximum value when the FeAs_4 tetrahedra are close to regular [22]. Deviation from the regular tetrahedron would lower T_c . Pressure will decrease the T_c of LiFeAs sample since it increases the deviation of FeAs_4 tetrahedra from regular.

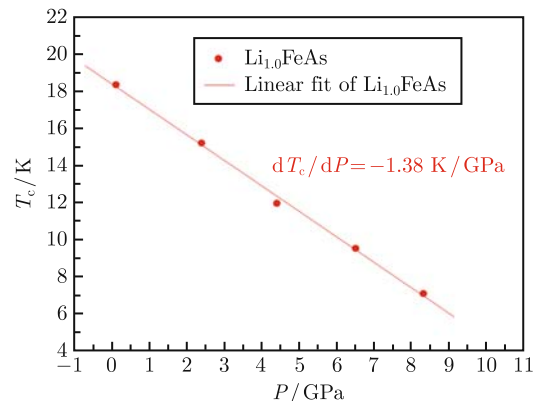


Fig. 5 Applied pressure dependence of T_c for samples with nominal composition $\text{Li}_{1.0}\text{FeAs}$.

Figure 6 shows the X-ray diffraction pattern for NaFeAs. The lattice parameters for NaFeAs at room temperature are $a = 3.955(3)$ Å and $c = 7.053(3)$ Å. The ρ - T curves and dc magnetic susceptibility for NaFeAs sample are shown in Fig. 7 and Fig. 8, respectively. The onset temperature T_ρ in Fig. 7 is defined with 26 K. Also there is no electric conductivity anomaly drop in the ρ - T curve for the NaFeAs sample. Considering the result that some evidence of SDW was observed for $\text{Na}_{1-\sigma}\text{FeAs}$ crystal [23], our NaFeAs sample might be doped. However, the onset temperature T_{M1} is defined with 11 K from Fig. 8. From the inset of Fig. 8 we can

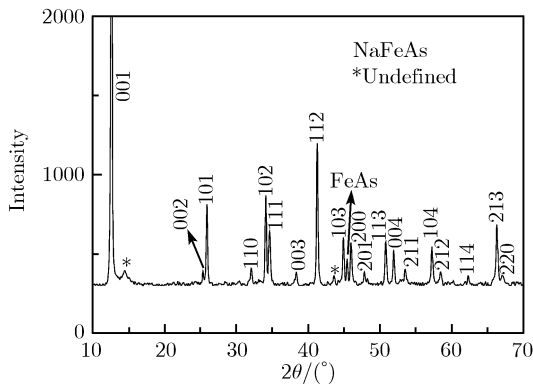


Fig. 6 The X-ray diffraction pattern of NaFeAs samples.

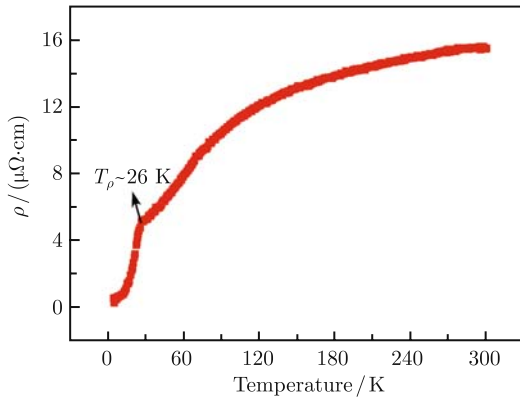


Fig. 7 The electric conductivity vs. temperature curve for NaFeAs sample.

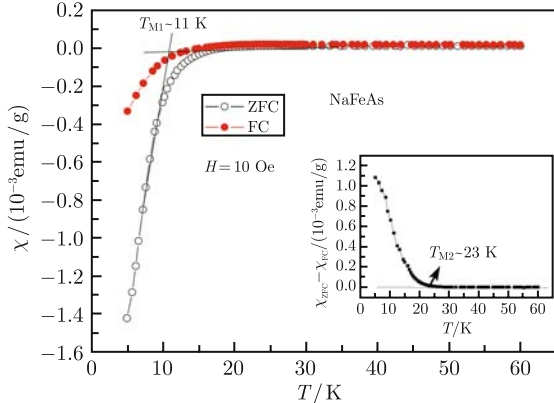


Fig. 8 The dc magnetic susceptibility for NaFeAs sample. Inset is the difference of FC and ZFC susceptibility.

obtain the temperature T_{M2} about 23 K, where the ZFC and FC curve converges. From the above data the critical superconducting temperature T_c for NaFeAs can be considered to be 23–26 K. Upon Li atoms being substituted by larger Na atoms in 111 type compounds, the As–Fe–As bond angle becomes 108.27° approaching to the bond angle of a regular tetrahedron. Considering that maximum T_c occurs when the FeAs_4 tetrahedra are close to the regular one as manifested in “1111” type compounds, it is justifiable that the T_c of NaFeAs should be higher than that of LiFeAs.

4 Conclusion

LiFeAs and NaFeAs samples are synthesized and show superconductivity with $T_c \sim 18$ K and 23–26 K, respectively. The T_c value of the LiFeAs sample decreases linearly with increasing pressure and the slope dT_c/dP is -1.38 K/GPa. There has been no evidence so far that SDW exists in LiFeAs compound.

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