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Alkali-metal Li and 1,3-diaminopropane intercalated superconductor $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ with $T_c\sim39$ K

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Abstract: A new FeSe-based superconductor $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ ($C_3H_{10}N_2$ refers to 1,3-diaminopropane) was successfully synthesized via the two-step method. This new material belongs to a tetragonal system and has a superconducting transition temperature (T_c) of 35 K. After annealing at 125 ℃ for 12 h, the crystal structure of this sample remained constant, but the T_c suddenly moved to 39 K, as confirmed by the powder X-ray diffraction and the magnetic susceptibility, respectively. Before and after annealing, the lattice constants a and b changed within 0.3 %, and the changes in c were slightly larger than 1 %. Therefore, it can be inferred that the evident change in T_c between as-synthesized and annealed samples should be attributed to a rearrangement and more homogeneous distribution of the intercalated guests.

Key words: FeSe-based superconductor; co-intercalated; annealed

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徐文涛,徐汉淑,曾涑源,等. 碱金属锂和1,3-丙二胺插层的超导体 $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ 具有 39 K 超导转变温度[J]. 中国科学技术大学学报,2019,49(6):439-4444.

碱金属锂和 1,3-丙二胺插层的超导体 $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ 具有 39 K 超导转变温度

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摘要:通过两步法成功合成了一种新的 FeSe 基超导体 $Li_x(C_3H_{10}N_2)_yFe_2Se_2$($C_3H_{10}N_2$ 指的是 1,3-丙二胺).这种新材料属于四方晶系,其超导转变温度为 35 K.在125℃退火 12h 后,该样品的晶体结构保持不变,但超导转变温度突然移至 39 K,这些均被粉末 X 射线衍射和磁化率测量证实.样品在退火前后,晶格常数 a 和 b 在 0.3%内变化,但是晶格常数 c 的变化约为 1%.因此,可以推断,样品的超导转变温度的明显变化应该归因于插层样品内部结构的重排和电子更均匀的分布.

关键词:FeSe 基超导体;共同插层;退火

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0 Introduction

In the last three decades, especially since the discovery of the copper oxide high transition temperature superconductor[1], the study of "unconventional" superconductivity has become one of the main topics in condensed matter physics. Among the unconventional superconductors[2-5], the β-FeSe has the simplest crystal structure composed of a stack of edge-sharing $FeSe_4$-tetrahedral layers and the T_c of bulk β-FeSe is highly tunable and can change from 8 K to over 40 K[6-7]. The preferred condition to increase the T_c of FeSe is by electron doping, which has been successfully realized via the interlayer intercalations[7], and interface charge transfer[8]. Therefore, finding an effective way to increase the T_c of FeSe-based superconductors has triggered a huge amount of innovative scientific inquiry.

Annealing is also one of the effective methods to improve the quality of samples and enhance T_c, due to the enhancement of crystallinity and the changes in the two-dimensionality of the electronic structure and the interlayer coupling of cooper pairs[9-10]. Compared with high pressure[11], molecular beam epitaxy (MBE)[8] and other technical means, annealing does not require overly-complex facilities, and most of scientific research groups can easily carry it out. For example, after high-pressure annealing of the as-synthesized FeSe-based superconductor $LiFeO_2Fe_2Se_2$, the T_c of this sample increased from 40 K to 43 K and the superconducting shielding fraction also improved significantly[12]. More interestingly, the T_c of a newly synthesized $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$ ($C_3H_{10}N_2$ refers to 1,2-diaminopropane) superconductor was directly increased from about 36 K to 45 K after annealing under vacuum, which was the first report of a significant increase in T_c just by annealing in FeSe-based superconductors[9]. Therefore, more new samples should be prepared to research the origin of high T_c mechanism. We want to change the composition of the intercalated samples, using the 1, 3-diaminopropane of 1, 2-diaminopropane isomer as a ligand to see if it can also synthesize samples with superconducting properties.

The two-step method (refering to chemical ultrasound reaction and solvothermal reaction) is a relatively effective chemical synthesis method for synthesizing high temperature FeSe-based superconducting materials, which have a purer crystal phase and a higher crystallinity[13]. Herein, we successfully synthesized a new superconductor $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ by the two-step process[13]. Post-annealing effects on the crystal structure and superconductivity were also discussed. It is found that the crystal structure maintains, which is confirmed by the powder X-ray diffraction, and that the as-obtained sample shows the T_c is 35 K, and the T_c of the annealed sample is 39 K, which is confirmed by the magnetic susceptibility measurement.

1 Experimental

1.1 Synthesis of FeSe

Predecessor of tetragonal FeSe was obtained by the traditional solid-state reaction method. A certain stoichiometric ratio of ferrous powder (99.99%, Alfa Aesar) and selenium particles (99.999%, Alfa Aesar) were mixed and placed into an alumina crucible in an argon-filled glove box and sealed in an evacuated quartz tube. The tube was sintered at 1050 ℃ and then cooled at a rate of 1 ℃ · min^{-1} to 410 ℃. At 410 ℃ the evacuated quartz tube was kept for 100 h. After being quenched in ice water, the black FeSe powder was obtained to be used for the intercalation.

2.2 Synthesis of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$

Polycrystalline samples of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ were prepared via the two-step method. 0.135 g FeSe powder and 0.07 g Li were put in 1, 3-diaminopropane in an ampule and sonicated for 3 h. Then the dispersed liquid was transferred to a Teflon-lined autoclave and heated at 130 ℃ for 3 d. After being washed repeatedly with the fresh 1,

3-diaminopropane and dried at room temperature, the $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ compound was obtained. All the processes were performed in an argon-filled glove box to prevent oxidation of the as-obtained samples. Post-annealing of the as-obtained samples was carried out at 125 ℃ for 12 h in a vacuum glass tube.

1.3 Characterization

The phase of samples was characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.5418 Å) of a Philips X-ray diffractometer. The magnetic susceptibility was measured using a commercial SQUID (Quantum Design). The chemical composition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and elemental analyzer (Vario EL III, Germany). Thermogravimetric (TG) analysis was performed on a simultaneous thermal analyzer (perkinelmer sta8000) from room temperature to 450 ℃ in a stream of N_2 with a heating rate of 10 ℃ · min^{-1}.

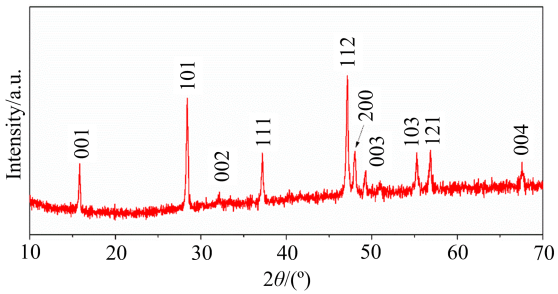


Fig. 1　Powder X-ray diffraction pattern of FeSe

2 Results and discussion

Fig. 1 shows the XRD pattern of the synthesized precursor FeSe. It can be inferred from the XRD pattern that the synthesized FeSe has a tetragonal structure of the anti-PbO-type. The unit cell parameters a = 3.772(2) Å and c = 5.526(3) Å. This is almost identical to what was reported in the previous literature, a = 3.770(1) Å and c = 5.521(8) A[13].

Fig. 2(a) shows the XRD pattern of the as-obtained $Li_x(C_3H_{10}N_2)_yFe_2Se_2$. All the diffraction peaks are well indexed to tetragonal lattice with cell parameters a = 3.793(1) Å and c = 9.263(2) Å, indicating that a pure phase of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ is prepared by the two-step method. Moreover, it is found that parameter a of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ is a little larger while parameter c is much larger than that of FeSe (a = 3.7676(2) Å, c = 5.4847(1) Å) respectively, implying that Li atoms and 1,3-diaminopropane molecules are independently intercalated into the interlayer space of FeSe. The intercalation of lithium and 1,3-diaminopropane were further affirmed by ICP-AES and elemental analyzer. The composition of the as-obtained sample can be estimated as $Li_{0.22}(C_3H_{10}N_2)_{0.49}Fe_2Se_2$. Compared with the alkali metal lithium and 1,2-diaminopropane co-intercalated $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$[9], parameter a is only slightly smaller, but parameter c decreases by 14 %, which would be assigned to the different types of organic amines as well as the different arrangement of organic amine molecules in FeSe layers in this work. However, compared with $Na_{0.85}(C_3H_{10}N_2)_{0.42}Fe_{1.84}Se_2$ (c = 10.000 Å)[14], parameter c is slightly reduced, which may be attributed to the fact that sodium ions are larger than lithium ions.

The XRD pattern for the annealed sample is shown in Fig. 2(b). It is found that the annealed sample retains the tetragonal crystal structure and the lattice constants (a = 3.803(1) Å, c = 9.363(4) Å) are a little larger than that of the as-obtained $Li_x(C_3H_{10}N_2)_yFe_2Se_2$, indicating that the sample has good thermal stability. In the previous reports, the annealing effect can affect the cell parameter c, which also shows that, to a certain extent, the cell parameter c is inclined to change[9-10]. From the XRD patterns of the as-synthesized and annealed samples, it can be clearly seen that the XRD diffraction peaks of the annealed sample become sharper, which indicates that the sample after annealing has better crystallinity[9-10].

In order to further confirm the content of organic amines, we performed a thermogravimetric analysis of the as-obtained sample. As shown in Fig. 3, the total mass loss is about 14.78 % after being heated up to 450 ℃ at a rate of 10 ℃ ·

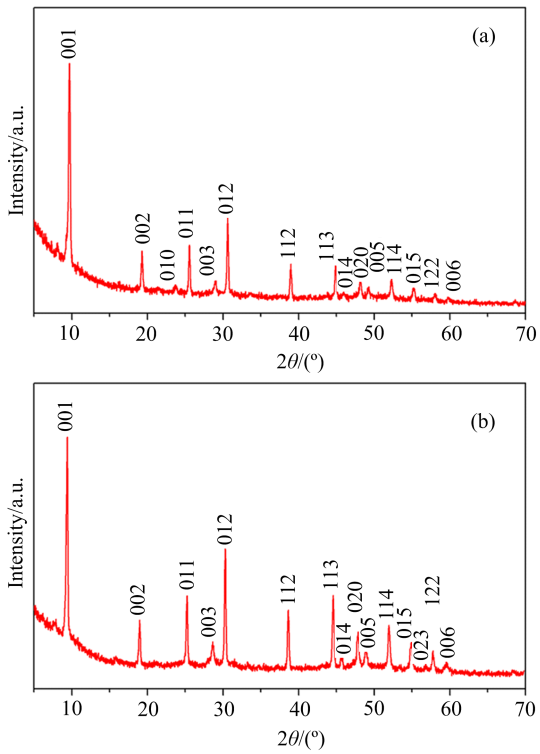


Fig. 2 Powder X-ray diffraction pattern for (a) the as-synthesized sample $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ and (b) the as-synthesized $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ sample annealed at 125 ℃ for 12 h

min^{-1}, which is a little larger than the mass fraction of organic amines, which is 11.80 % as estimated by the elemental analyzer. The mass loss is divided into two steps. During the first step, the mass loss is about 7 % below 120 ℃, which may be associated with the small amount of water, 1,3-diaminopropane on the surface and in the internal of as-obtained $Li_{0.22}(C_3H_{10}N_2)_{0.49}Fe_2Se_2$. After the second step, between 120～320 ℃, the mass loss reaches 14.78 % and is not further decreased at a higher temperature, indicating that the 1,3-diaminopropane is almost all detached from the as-obtained sample[10].

Fig. 4(a) displays the temperature dependence of magnetic susceptibility in a magnetic field of 10 Oe on zero-field cooling (ZFC) and field cooling (FC) for the as-obtained $Li_x(C_3H_{10}N_2)_yFe_2Se_2$. The T_c is observed at 35 K, which is higher than that of pure FeSe[15], but is slightly lower than $T_c=36.7$ K observed in FeSe under pressure[6]

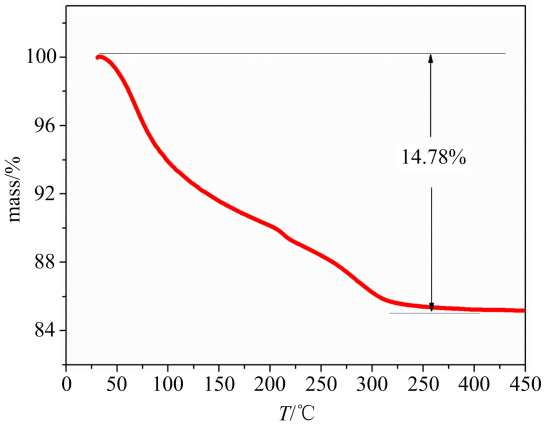
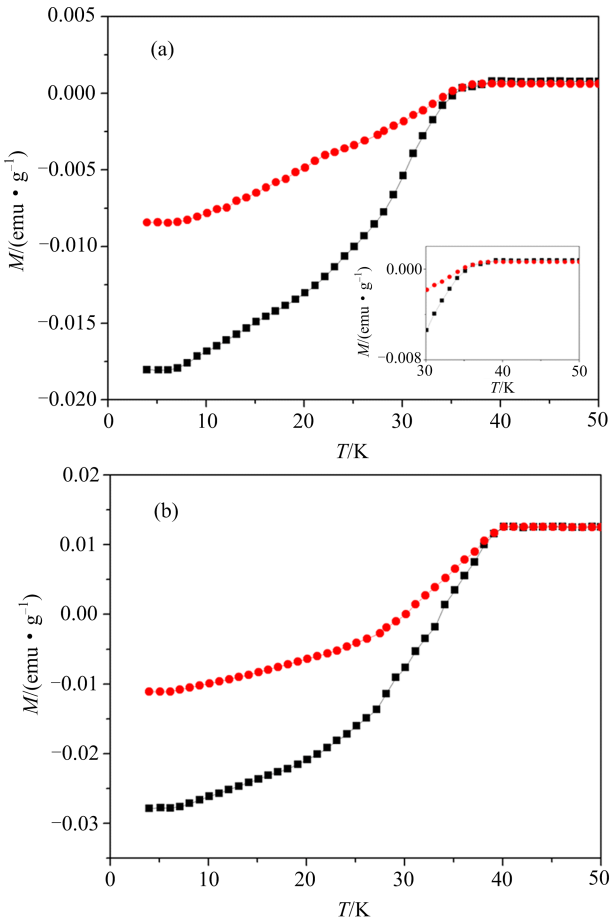


Fig. 3 Thermogravimetric (TG) curve on heating at the rate of 10 ℃ · min^{-1} for the as-synthesised sample



(a) The magnetic susceptibility of the as-synthesized $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ sample in a magnetic field of 10 Oe on zero-field cooling (ZFC: square symbols) and field cooling (FC: circular symbols). The inset shows an expanded view around the superconducting transition of the as-synthesized sample. (b) The magnetic susceptibility of the annealed sample.

Fig. 4 The magnetic moment of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ superconductor

and $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$ ($T_c=36.7$ K)[9]. It

is noted that the magnetic susceptibility curve exhibits an upturn below 6 K, which may have been caused by a small amount of magnetic impurities in the sample[9,16-17]. Considering the previous reports, it is found that the post-annealing process can affect the T_c of the samples. For example, the T_c of $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$ prepared by the co-intercalation of alkali metal lithium and 1, 2-diaminopropane increases from 36.7 K to 45 K after being annealed at 130 ℃[9]. Moreover, $Li_x(C_6H_{16}N_2)_yFe_{2-z}Se_2$ displays a change of T_c while being annealed at a different temperature from 100 ℃ to 250 ℃[10]. In order to investigate the effects of annealing on the T_c, we characterized the magnetic susceptibility of the $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ after being post-annealing at 125 ℃ for 12 h. As shown in Fig. 4(b), the T_c of the annealed sample slightly increases to 39 K. The change of T_c of the as-obtained and annealed samples could be assigned to a rearrangement and more homogeneous distribution of 1, 3-diaminopropane in the intercalated compound[9]. Meanwhile, parameter c of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ has a little change after being annealed, which would lead the interlayer coupling of cooper pairs and the two-dimensionality in the electronic structure to change, and thus affects the superconducting transition temperature[9]. However, the T_c is significantly smaller than that of the annealed $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$ (T_c = 45 K), which may be due to the higher concentration of lithium ions in the $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$[9]. The increase in electron concentration increases the T_c of the intercalation compounds[18]. And the superconducting transition temperature of $Li_{0.27}(C_3H_{10}N_2)_{0.31}Fe_2Se_2$ ($C_3H_{10}N_2$ refers to 1,2-diaminopropane) is 37 K[13], which also proves that the electron concentration has a certain influence on the superconducting transition temperature. Compared to the $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$[9], the decrease of the layer spacing of the sample may also cause the superconducting transition temperature to be less than $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$. The magnetic susceptibility at the normal state is positive, indicating that the as-obtained and annealed samples contain a small amount of ferromagnetic impurities derived from Fe species extracted from the samples during the intercalation process or impurity phase induced by the heat treatment[9-10,19-20] This behavior has also been observed in $A_x(C_2H_8N_2)_yFe_{2-z}Se_2$ (A = Li, Na)[19], $A_x(C_5H_5N)_yFe_{2-z}Se_2$[20] and $Li_{0.36}(C_3H_{10}N_2)_{0.42}Fe_2Se_2$[9].

Based on this newly synthesized sample, we have expanded the class of FeSe-based superconductors. The iron-molecular-based intercalation can enrich the iron-based superconducting system and even the materials of other systems to further improve the superconducting properties. In addition, it also helps to study the basic physics of iron-based high T_c superconductors. Although the sample can not yet be used in actual life due to its sensitivity to air and moisture, we should still prepare more valuable samples.

3 Conclusion

In summary, we successfully synthesized a new phase compound of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ ($C_3H_{10}N_2$ refering to 1, 3-diaminopropane) by the two-step process. The as-synthesized $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ has a tetragonal crystal structure and a superconducting transition temperature of 35 K. After annealing at 125 ℃ for 12 h, the superconducting transition temperature of $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ has slightly increased from 35 K to 39 K, which is confirmed by the magnetic susceptibility result. At the same time, it is found that the crystal structure of the $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ remains after annealing, which is confirmed by the powder X-ray diffraction result. Consequently, in this work, a novel FeSe-based intercalated compound was synthesized and gives a further understanding of alkali metal/alkaline earth metal and organic amine solution co-intercalated FeSe materials.

References

[1] BEDNORZ J G, MÜLLER K A. Possible high T_c superconductivity in the Ba-La-Cu-O system [J].

Zeitschrift für Physik B Condensed Matter, 1986, 64: 189-193.

[2] MAENO Y, HASHIMOTO H, YOSHIDA K, et al. Superconductivity in a layered perovskite without copper [J]. Nature, 1994, 372: 532-534.

[3] MACKENZIE A P, MAENO Y. The superconductivity of Sr_2RuO_4 and the physics of spin-triplet pairing [J]. Reviews of Modern Physics, 2003, 75(2): 657.

[4] STEGLICH F, AARTS J, BREDL C D, et al. Superconductivity in the presence of strong Pauli paramagnetism: $CeCu_2Si_2$ [J]. Physical Review Letters, 1979, 43: 1892.

[5] KAMIHARA Y, WATANABE T, HIRANO M, et al. Iron-based layered superconductor La[$O_{1-x}F_x$]FeAs (x=0.05−0.12) with T_c= 26 K [J]. Journal of the American Chemical Society, 2008, 130: 3296-3297.

[6] MEDVEDEV S, MCQUEEN T M, TROYAN I A, et al. Electronic and magnetic phase diagram of β-$Fe_{1.01}Se$ with superconductivity at 36.7 K under pressure [J]. Nature materials, 2009, 8: 630-633.

[7] BURRARD-LUCAS M, FREE D G, SEDLMAIRE S J, et al. Enhancement of the superconducting transition temperature of FeSe by intercalation of a molecular spacer layer [J]. Nature Materials, 2013, 12: 15-19.

[8] WANG Q Y, LI Y, ZHANG W H, et al. Interface-induced high-temperature superconductivity in single unit-cell FeSe films on $SrTiO_3$ [J]. Chinese Physics Letters, 2012, 29: 037402.

[9] XU H S, WANG X X, GAO Z, et al. New alkali-metal and 1, 2-Diaminopropane intercalated superconductor $Li_x(C_3H_{10}N_2)_yFe_2Se_2$ with T_c=45 K [J]. Journal of Alloys and Compounds, 2018, 735: 2053-2057.

[10] HOSONO S, NOJI T, HATAKEDA T, et al. New superconducting phase of $Li_x(C_6H_{16}N_2)yFe_{2-z}Se_2$ with T_c = 41 K obtained through the post-annealing [J]. Journal of Physics Society of Japan, 2016, 85: 013702.

[11] SUN J P, MATSUURA K, YE G Z, et al. Dome-shaped magnetic order competing with high-temperature superconductivity at high pressures in FeSe [J]. Nature Communications, 2016, 7: 12146.

[12] LU X F, WANG N Z, ZHANG G H, et al. Superconductivity in $LiFeO_2Fe_2Se_2$ with anti-PbO-type spacer layers [J]. Physical Review B, 2014, 89: 020507(R).

[13] XU H S, WANG X X, TANG L L, et al. New synthetic route to synthesize Li and 1, 2-diaminopropane-intercalated iron-based superconductor with T_c = 37 K [J]. ChemistrySelect, 2018, 3(27): 7757-7762.

[14] HAYASHI F, LEI H C, GUO J G, et al. Modulation effect of interlayer spacing on the superconductivity of electron-doped FeSe-based intercalates [J]. Inorganic Chemistry, 2015, 54: 3346-3351.

[15] HSU F C, LUO J Y, YEH K W, et al. Superconductivity in the PbO-type structure α-FeSe [J]. Proceedings of the National Academy of Sciences of the United Sates of America, 2008, 105: 14262-14264.

[16] HOSONO S, NOJI T, HATAKEDA T, et al. New alkali-metal- and 2-phenethylamine-intercalated superconductors $A_x(C_8H_{11}N)_yFe_{1-z}Se$ (A=Li, Na) with the largest interlayer spacings and Tc~40 K [J]. Journal of Physics Society of Japan, 2016, 85: 103702.

[17] PACHMAYR U, NITSCHE F, LUETKENS H, et al. Coexistence of 3d-ferromagnetism and superconductivity in $[(Li_{1-x}Fe_x)OH](Fe_{1-y}Li_y)Se$ [J]. Angewandte Chemie International Edition, 2015, 544: 293-297.

[18] YING T P, CHEN X L, WANG G, et al. Superconducting phases in potassium-intercalated iron selenides [J]. Journal of the American Chemical Society, 2013, 135: 2951-2954.

[19] HATAKEDA T, NOJI T, HOSONO S, et al. Resistive superconducting transition and effects of atmospheric exposure in the intercalation superconductor $A_x(C_2H_8N_2)_yFe_{2-z}Se_2$ (A=Li, Na) [J]. Journal of Physics: Conference Series, 2014, 568: 022032.

[20] KRZTON-MAZIOPA A, POMJAKUSHINA E V, POMJAKUSHIN V Y, et al. Synthesis of a new alkali metal-organic solvent intercalated iron selenide superconductor with $T_c \approx$ 45 K [J]. Journal of Physics: Condensed Matter, 2012, 24: 382202.