Observation of superconductivity at
30–46 K in \( A_xFe_2Se_2 \) (\( A = \text{Li, Na, Ba, Sr, Ca, Yb, and Eu} \))

T. P. Ying, X. L. Chen, G. Wang, S. F. Jin, T. T. Zhou, X. F. Lai, H. Zhang & W. Y. Wang

Research & Development Center for Functional Crystals, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

New iron selenide superconductors by intercalating smaller-sized alkali metals (Li, Na) and alkaline earths using high-temperature routes have been pursued ever since the discovery of superconductivity at about 30 K in KFe\(_2\)Se\(_2\), but all have failed so far. Here we demonstrate that a series of superconductors with enhanced \( T_c \) of 30–46 K can be obtained by intercalating metals, Li, Na, Ba, Sr, Ca, Yb, and Eu in between FeSe layers by the ammonothermal method at room temperature. Analysis on their powder X-ray diffraction patterns reveals that all the main phases can be indexed based on body-centered tetragonal lattices with \( a = 3.755–3.831 \) Å while \( c = 15.99–20.54 \) Å. Resistivities show the corresponding sharp transitions at 45 K and 39 K for NaFe\(_2\)Se\(_2\) and Ba\(_{0.8}\)Fe\(_2\)Se\(_2\), respectively, confirming their bulk superconductivity. These findings provide a new starting point for studying the properties of these superconductors and an effective synthetic route for the exploration of new superconductors as well.

The discovery of superconductivity (SC) at about 30 K in K\(_{0.8}\)Fe\(_{1.7}\)Se\(_2\), and subsequently in Rb\(_{0.8}\)Fe\(_{1.7}\)Se\(_2\), Cs\(_{0.8}\)Fe\(_{1.7}\)Se\(_2\), (Tl,K)Fe\(_{2}\)Se\(_2\), and (Tl,Rb)Fe\(_{2}\)Se\(_2\) has aroused a surge of research interests as these iron chalcogenides possess a strikingly distinct electronic structure from their iron pnictide counterpart superconductors. Angle-resolved photoemission spectroscopy studies revealed that only electron Fermi surfaces are observed around the zone corners while no hole Fermi surface near the zone centre, implying that interband scattering or Fermi surface nesting is not a dominant pairing mechanism. X-ray and neutron diffraction studies indicated that all these superconductors are close to Am\(_{0.8}\)Fe\(_{1.6}\)Se\(_2\) (Am = K, Rb, Cs, and Tl) in composition with Fe vacancies ordering to form a \( \sqrt{5} \times \sqrt{5} \times 1 \) supercell below the order-disorder transition temperatures, but the phase responsible for the SC is still in debate. Moreover, a trace fraction of SC at 44 K was occasionally observed in an unknown phase coexisting with K\(_{0.8}\)Fe\(_{2}\)Se\(_2\). Efforts to synthesize new isostructural chalcogenides with other alkali metals and alkaline earths for clarifying the superconducting phase and exploring new superconductors have failed up to now.

Liquid ammonia (LA) is known to dissolve alkali metals, alkaline earths, and even some rare earths to varying extents. Intercalating alkali metals, alkaline earths, rare earth Yb, and ammonia into MoS\(_2\) and C\(_{60}\) yields superconductors, respectively. Here we report that metals, Li, Na, Ba, Sr, Ca, Yb, and Eu can be intercalated in between FeSe layers by the ammonothermal method and form a series of superconductors with enhanced \( T_c \) of 30–46 K, which cannot be obtained by similar high-temperature routes described in ref. 1. These results demonstrate that metal intercalations at low temperatures are possible with the aid of ammonia and SC can be induced by electron doping through intercalating a variety of metals. Our findings provide a new starting point for further exploring the SC and mechanism in the metal-doped iron selenides.

Results

Figure 1 shows the powder X-ray diffraction patterns for nominal A\(_x\)Fe\(_2\)Se\(_2\) (\( A = \text{Li, Na, K, Ba, Sr, Ca, Yb, and Eu} \)). The patterns for FeSe and K\(_{0.8}\)Fe\(_{1.7}\)Se\(_2\) that were obtained by high-temperature route are also included for comparison. Trying to index each pattern based on a single crystallographic unit cell only succeeds for LiFe\(_2\)Se\(_2\), NaFe\(_2\)Se\(_2\), and Ba\(_{0.8}\)Fe\(_2\)Se\(_2\), while patterns for KFe\(_2\)Se\(_2\), Ca\(_{0.8}\)Fe\(_2\)Se\(_2\), Sr\(_{0.8}\)Fe\(_2\)Se\(_2\), EuFe\(_2\)Se\(_2\), and Yb\(_{0.8}\)Fe\(_2\)Se\(_2\) yield more than one crystallographic unit cell. The patterns for LiFe\(_2\)Se\(_2\), NaFe\(_2\)Se\(_2\), and Ba\(_{0.8}\)Fe\(_2\)Se\(_2\) were indexed on body-centered tetragonal cells with lattice constants \( a = 3.775(5) \) Å, \( c = 17.04(3) \) Å; \( a = 3.784(6) \) Å, \( c = 17.432(1) \) Å; and \( a = 3.778(12) \) Å, \( c = 16.842(7) \) Å, respectively. All constants ‘a’ are comparable with that of K\(_{0.8}\)Fe\(_{1.7}\)Se\(_2\) by the high-temperature route while ‘c’ being elongated. Since the much elongated unit cell along...
the c axis, in between the FeSe layers should exist other atomic groups relating with NH₃ apart from the intercalated metals. Considering the relatively little contribution to the peak intensity from N and H and the heavy absorption of the Cu Kα radiation by Fe, we first performed Rietveld refinements for nominal NaFe₂Se₂ based on the I₄/mmm structural model of K₀.₈Fe₂Se₂ and the final agreement factors converged to R_p = 2.18%, R_wp = 3.05%, and R_exp = 1.77%. Trying on the model proposed for Liₓ(NH₂)ₓ(NH₃)₁₋ₓFe₂Se₂ does not improve the refinement, only leading to a slight increase in agreement factors. Based on K₀.₈Fe₂Se₂ model, the final refined parameters are summarized in Table I. As shown in the inset of Fig. 2, the crystal structure obtained from the refinement is composed of edge-sharing FeSe₄-tetrahedra layers separated by Na. The Fe-Se and Fe-Fe bond lengths according to the refined parameters are 2.362(₄) Å and 2.676(₃) Å, respectively, shrinking a lot compared over with 2.4406(₄) Å and 2.767₃(₅) Å for K₀.₈Fe₂Se₂. Bond angles, however, show only slight changes. Similarly, the refinement results for Ba₀.₈Fe₂Se₂ are shown in Supplementary Figure S1 and Table SI.

Indexing the pattern for KFe₂Se₂ by the ammonothermal method yields two body-centered tetragonal cells with lattice constants a = 3.755(3) Å and c = 20.4₂₂(1) Å, and another with lattice constants a = 3.7₉(2) Å and c = 16.1₆(5) Å. Similar situation applies to Ca₀.₅Fe₂Se₂, Sr₀.₈Fe₂Se₂, EuFe₂Se₂, and Yb₀.₈Fe₂Se₂, in which the main diffraction peaks can be indexed based on two body-centered tetragonal cells. This multi-phase nature reflects the inhomogeneity of these samples for the intercalation process is diffusion controlled. All the indexing results are listed in Supplementary Table SII.

Examination of the intercalated compounds reveals that all the lattice constants a expand, while c are nearly tripled or even larger compared over β-FeSe. This result along with the chemical analysis (see Table II) indicates that the metals are indeed intercalated in between FeSe layers and form new layered compounds similar to K₀.₈Fe₁.₇Se₂ by the high-temperature route in structure. But the inserting amounts are varying from metal to metal.

The magnetism of samples was measured as a function of temperature or magnetic field. Shown in Fig. 3 are the M-T curves for nominal NaFe₂Se₂ under zero field and a field of 40 Oe cooling, respectively. Over the temperature range from room temperature to the onset transition temperature, zero-field-cooling (ZFC) and field-cooling (FC) curves are quite flat and nearly temperature independent, implying little or no magnetic impurity (β-FeSe, Fe₇Se₈, Fe and etc.) in the sample. The curves sharply drop in both ZFC and FC.

Table I | Crystallographic data and Rietveld refinement data for NaFe₂Se₂

| Temperature (K) | Space group | Fw | a (Å) | c (Å) | V (Å³) | Z | R_p | R_wp | R_exp | GoF-index |
|----------------|-------------|----|-------|-------|--------|---|------|------|--------|-----------|
| 297            | I₄/mmm      | 292.6 | 3.78₄₆(⁴) | 17.₄₃₂(1) | 249.₆₉₄(⁴) | 2 | 2.18% | 3.05% | 1.₇₇% | 1.₇       |

 Atomic parameters

| Na  | 2a (0, 0, 0) | 0.₆₇(2) |
| Fe  | 4d (0, 0.₅, 0.₂₅) | 4e (0, 0, z) | z = 0.₃₃₁₁(₄) |
| Se  | z = 0.₃₃₁₁(₄) | 2.₆₇₆ (₃) |

Bond lengths (Å)

| Na-Se | 3.₉₇₇ (₅) x 8 |
| Fe-Se | 2.₃₆₂ (₄) x 4 |
| Fe-Fe | 2.₆₇₆ (₃) x 4 |

Bond angles (deg.)

| 1₁₁₁.₀ (₁) x 4 | 1₇₀.₆ (₂) x 2 |

Figure 1 | Powder X-ray diffraction patterns for samples measured at 297 K, Cu Kα radiation. (a) β-FeSe; (b) K₀.₈Fe₁.₇Se₂ (by high-temperature route); (c) Nominal LiFe₂Se₂; (d) Nominal NaFe₂Se₂; (e) Nominal KFe₂Se₂ (background corrected), peaks marked by ‘.’ are due to unknown phase; (f) Nominal Ca₀.₅Fe₂Se₂; (g) Nominal Sr₀.₈Fe₂Se₂; (h) Nominal Ba₀.₈Fe₂Se₂; (i) Nominal EuFe₂Se₂; (j) Nominal Yb₀.₈Fe₂Se₂. Peaks marked by ‘*’ are due to residual β-FeSe.
signaling a SC transition begins at about 46 K, comparable to 48.7 K observed in $K_{0.8}Fe_{1.7}Se_2$ under a pressure of 12.5 GPa. To confirm the SC transition, we measured its M-H curves at 10 K and 60 K and $\rho$-$T$ curve (see inset of Fig. 3). The M-H curve at 10 K exhibits clear magnetic hysteresis, a typical feature of type-II superconductor. The superconductive shielding fraction is estimated to be about 40% at 10 K. A sharp transition in electrical resistance at 45 K is observed though not reaching zero resistance as the sample is cold pressed, further confirming the SC transition. Figure 4a shows the M-T curves for nominal $Ba_{0.8}Fe_2Se_2$, very similar to the ones for NaFe$_2$Se$_2$, except for the transition temperature that is lowered to 39 K. The estimated superconductive shielding fraction is about 62% at 10 K. Shown in the inset of Fig. 4a are M-H curves and $\rho$-$T$ curve of $Ba_{0.8}Fe_2Se_2$, confirming its SC transition and the type-II superconductor again. Its lower critical field ($H_{c1}$) is around 0.15 T and the estimated upper critical filed ($H_{c2}$) is about 36.5 T (see Supplementary Fig. S2). Figure 4b shows the heat capacity of cold-pressed powder $Ba_{0.8}Fe_2Se_2$. In the normal state, the electronic coefficient of heat capacity $c$ is determined to be $3.47 \times 10^{-3} \text{ mJ g}^{-1} \text{ K}^{-2}$ according to the zero-temperature intercept. At lower temperatures, no apparent peak is present, but a clear deviation from the linear change at 39 K is observed, again confirming the nature of bulk SC in $Ba_{0.8}Fe_2Se_2$. For all other samples, the M-T and M-H curves can be seen in Fig. 5. In particular, we note that the Li insertion leads to SC at 44 K, in
contrast to the previous report that Li intercalation into Fe(Se,Te) has no effect on SC and structure. Further work is underway to clarify the structure and property of these new superconductors.

Some samples obtained by the ammonothermal method are sensitive to atmosphere. Magnetization measurements on sample KFe2Se2 show its SC transition temperature changes from 40 K to 30 K after one hour’s exposure to air (see Supplementary Fig. S3), accompanying the disappearance of one body-centered tetragonal cell with lattice constants a = 3.755(3) Å, c = 20.48(1) Å shown in Supplementary Fig. S4. Others, however, are relatively stable. For example, the SC transition temperature for Ba0.5Fe2Se2 shows no apparent change after several hours in air and 4 days in glove box, only a 4 K drop after annealing at 373 K for 3 days (see Supplementary Fig. S5). The powder diffraction patterns (see Supplementary Fig. S6) show that only the impurity Ba(OH)2 turns into Ba(OH)2·H2O after air exposure and annealing, while the diffraction peaks corresponding to Ba0.5Fe2Se2 show no apparent change. NH3 is possible to enter in between the layers as observed in MoS224 and C6030,31. But infrared spectroscopy measurements on our samples do not show clear peak due to N-H vibrations (see Supplementary Fig. S7) and the role of NH3 in inducing SC is not clear, which is inconsistent with the recent report of Li(x)(NH2)y(NH3)1-yFe2Se2 in which lithium ions, lithium amide and ammonia are intercalated into FeSe layers.26 The SC of samples only soaking in LA without addition of metal has not been confirmed above 10 K.

Discussion

The refined structures manifest that Na and Ba are intercalated in between FeSe layers. But it is hard to understand why their lattice
parameters $c$ are much elongated compared with the $c$ for $K_{0.8}Fe_2Se_2$. This is, in particular, true for $NaFe_2Se_2$ as $Na$ has a smaller ionic radius than $K$ has. One plausible explanation is that in between $FeSe$ layers there exist other atoms or atomic groups such as $NH_3$, $NH_2$ apart from $Na$ and $Ba$, though infrared spectra do not show the vibration peak due to N-H bond. Their accurate structures, however, need to be confirmed by other experimental means in future. In addition, we note that the refined $Ba$ occupancy is quite low as 0.212(3), less than half of that for $Na$ in $NaFe_2Se_2$. This is reasonable from the point of charge transfer view since its normal valence is $+2$.

Hence, SC at 30–46 K in these intercalated iron selenides is believed to be induced by high electron doping from the metals intercalated to $FeSe$ layers, which has been previously proved in $Am_{0.8}Fe_2Se_2^{1-7}$ ($Am=K$, Rb, Cs, and Tl). Further work is presently underway to understand the differences between the structure and onset transition temperatures for the $Li$, $Na$, $Ba$, $Sr$, $Ca$, $Yb$, and $Eu$ intercalated superconductors. Although here we have focused on the intercalation of alkali metals, alkaline earths, and some rare earths, the approach to intercalate other spacer layers and to synthesize from solvents other than LA should also be possible to adopt in future. In particular, layered compounds with layer spacings large enough are promising parent targets to obtain new superconductors with possible higher $T_c$.

In summary, we have obtained a series of new superconductors through the ammonothermal method at room temperature. A
In this work, we first synthesized the M-FeSe system induced by doping. The results presented here demonstrate that superconductors are rich in variety of metals are verified to be intercalated in between FeSe layers following the method described in ref. 1. Alkali metals, alkaline earths, Yb, Eu, and FeSe powder in molar ratios A/β-FeSe = (0.5–1) were loaded in a 23 ml or 50 ml autoclave which was placed in a bath of liquid nitrogen for 2–3 minutes and then LA (99.999%) was slowly filled up to the 1/3–1/2 volume of the autoclave with the concentrations of metals solved in LA reaching about 0.1–0.3 atomic %. All the conductors were performed under Ar atmosphere in a glove box to prevent air and water contamination. After sealed, the autoclaves were taken out and kept at room temperature for 2–17 days. During the process, shaking was needed to facilitate the reaction and to improve the homogeneity of the products. Finally, the samples were rinsed by using fresh LA to eliminate soluble impurities. All the samples’ nominal compositions, masses of starting materials, and synthetic conditions are listed in Table II. Cautionary note: caution should be taken to avoid frostbite by LA.

The samples were characterized by powder X-ray diffraction using a PANalytical XPert PRO diffractometer with Cu Kα radiation. Indexing was performed with DICOVLO64. Rietveld refinements of the diffraction data were performed with the FULLPROF package65. The magnetic and transport properties were characterized using a vibrating sample magnetometer (VSM, Quantum Design) and the physical property measurement system (PPMS, Quantum Design), respectively. The magnetic measurements were carried out in the field of 40 Oe in the temperature range 5–300 K after cooling in zero field and in the measuring field. The electrical resistances were measured by using the standard four-probe method based on samples cold-pressed at a uniaxial stress of 400 kg cm⁻². The low temperature heat capacity was measured on the superconductor revealed by angle-resolved photoemission spectroscopy. The magnetic and transport properties of the potassium-intercalated iron selenide KₓFe₂-ySe₂. A novel large moment antiferromagnetic order in KₓFe₂-ySe₂ superconductor revealed by angle-resolved photoemission spectroscopy. The magnetic and transport properties of the potassium-intercalated iron selenide KₓFe₂-ySe₂. A novel large moment antiferromagnetic order in KₓFe₂-ySe₂ superconductor. 8. Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. Iron-based superconductor La(O₁₋ₓFx)FeAs (x = 0.05–0.12) with Tc = 26 K. J. Am. Chem. Soc. 130, 3296–3297 (2008).
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Author contributions

T.P.Y. did most of the synthesis and characterizations. X.L.C. designed the experimental scheme. X.L.C. and G.W. analysed the data and wrote the paper. S.F.J. did the structure analysis. T.T.Z., X.F.L., H.Z., and W.Y.W. helped with the experiment.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

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