A new series of superconductors, with the general formula, 

$$A_xFeSe_2$$

has been recently identified and shown to have significantly enhanced superconducting transition temperatures ($T_c$ up to 32 K$^3$) as compared to FeSe ($T_c = 8.5$ K$^2$). This series joins a growing list of pnictide and chalcogenides superconductors that include the original ZrCuSiAs-type compounds, such as LnO$_x$Fe$_4$As$_3$$^9$,$^{19}$ where Ln is a lanthanide ion, the ThCr$_2$Si$_2$-type structures of AFe$_2$As$_2$, where A is aalkali or alkaline earth metal,$^{10,12}$ and the anti-PbFCl structure of AFeAs, where A is analkaline metal,$^{13}$,$^{14}$ All of these compounds contain iron in tetrahedral coordination that are edge-shared to form two-dimensional structures. The simplest of the chalcogenides are those with the anti-PbO structure with the general formula, Fe$_{1+y}$(Te, Se, S). FeSe is superconducting at 8.5 K$^2$ and is very sensitive to interstitial iron ions.$^{15}$ Fe$_{1+y}$Te, where x lies between 0.076 and 0.18, shows commensurate or incommensurate antiferromagnetism depending on exact composition.$^{16}$ The antiferromagnetism can be suppressed and superconductivity emerges on substituting some Te with either Se$^{17,18}$ or S$^{19}$. In both cases, thechemical pressure afforded by the Se$^{20}$ and S$^{21}$ inclusion reduces the amount of interstitial iron. The amount of the interstitial iron can be reduced by topotactic deintercalation using iodine$^{22}$. Fe$_{1+y}$Te$_{0.5}$Se$_{0.5}$ was shown to transform from gapless paramagnetism to superconductivity on Fe removal$^{23}$.

The superconducting K-Fe-Se phases were found to possess the ThCr$_2$Si$_2$ structure and isostructural with AFe$_2$As$_2$. The first structure determination of AFeSe in this layered tetragonal arrangement was with A as the group 13 metal, TI. It possesses lattice parameters of $a = b = 3.890(1)$ Å and $c = 14.00(1)$ Å and was shown to be a p-type Pauli paramagnetic metal$^{24-26}$. A related composition was shown to be antiferromagnetic at $T_N \approx 450$ K and have ordered Fe vacancies, which is best described as TiFe$_2$.Se$_2$ with a $\sqrt{5} \times \sqrt{5} \times 1$ supercell giving a 5 fold volume increase at $x \approx 0.3$. Superconducting potassium iron selenide was first reported above 30 K in K$_3$Fe$_2$Se$_2$, which has K deficiency, but stoichiometric Fe and Se, and lattice parameters of $a = 3.9136(1)$ Å and $c = 14.0367(7)$ Å$^1$. Similar properties have also been reported in iron deficient (TI,K)Fe$_2$.Se$_2$,$^{28}$alkali metal deficient Rb$_3$.Fe$_2$.Se$_2$,$^{29}$ K$_3$.Fe$_2$.Se$_2$,$^{30}$ and K$_3$.Fe$_2$.Se$_2$,$^{31}$ and alkali metal and Se deficiency Rb$_3$.Se$_2$,$^{32}$ and Cs$_3$.Fe$_2$.Se$_2$,$^{33}$.

As a result of both the chemical importance of interstitial iron in the Fe$_{1+y}$(Te, Se, S) series and the variation in properties in the A$_x$Fe$_2$Se$_2$ series warrants careful determination of the exact stoichiometry of these superconductors. In a single crystal X-ray diffraction structure determination, we observe that in superconducting samples of composition, K$_{0.774(4)}$.Fe$_{1.613(2)}$.Se$_2$, K$_{0.738(4)}$.Fe$_{1.513(1)}$.Se$_2$ and Cs$_{0.749(2)}$.Fe$_{1.626(1)}$.Se$_2$, with a near perfect diamagnetic response$^{34}$, an ordered vacancy structure that contains both alkali metal and iron deficiencies to form an ordered (5x 5x 1) superlattice, which is consistent with a recent transmission electron microscope study that reports a superstructure modulation along the [310] direction,$^{35}$ as well as powder neutron diffraction$^{36}$. The structure is related to a recent X-ray diffraction study of non-superconducting K$_{0.8}$.Fe$_{1.8}$.Se$_2$, but here we show that the superconducting composition contain one occupied and one vacant site, rather than two partially occupied Fe sites$^{37}$. The complexity of the structure demonstrates the need to map out the iron selenide

**On the Structure of Vacancy Ordered Superconducting Alkali Metal Iron Selenide**

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With single crystal X-ray diffraction studies, we compare the structures of three sample showing optimal superconductivity, K$_{0.774(4)}$.Fe$_{1.613(2)}$.Se$_2$, K$_{0.738(4)}$.Fe$_{1.513(1)}$.Se$_2$ and Cs$_{0.749(2)}$.Fe$_{1.626(1)}$.Se$_2$. All have an almost identical ordered vacancy structure with a (5x 5x 1) super cell. The tetragonal unit cell, space group I4/m, possesses lattice parameters at 250K of $a = b = 8.729(2)$ Å and $c = 14.120(3)$ Å, $a = d = 8.7136(12)$ Å and $c = 14.0853(19)$ Å and at 295 K, $a = b = 8.6617(16)$ Å and $c = 15.304(3)$ Å for the three crystals, respectively. The structure contains two iron sites; one is almost completely empty, whilst the other is fully occupied. There are similarly two alkali metal sites that are occupied in the range of 72.2(2) % to 85.3(1) %. The inclusion of alkali metals and the presence of vacancies within the structure allows for considerable relaxation of the FeSe$_2$ tetrahedron, compared with members of the Fe(Te, Se, S) series, and the resulting shift of the Se – F – Se bond angles to less distorted geometry could be important in understanding the associated increase in the superconducting transition temperature. The structure of these superconductors distinguishes themselves from the structure of the non-superconducting phases by an almost complete absence of Fe on the (0 0.5 0.25) site as well as lower alkali metal occupancy that ensures an exact Fe$^{2+}$ oxidation state, which are clearly critical parameters in the promotion of superconductivity.
The 25 times cell suggested a reduced irreducible representation analysis of the magnetic structure in group, using the original composition in these systems diffraction data, which can very accurately determine Fe and powder neutron diffraction data suggested limited iron site disorder from partial occupancy in consis for sites; resulting structure latter was selected based on the intensity statistics. Th performed in the super cell within space group I4/mmm. The ThCr indexed on a given in crystal structure reports in supplementary information. tube (\(\lambda = 0.71073 \, \text{Å}\)).

On the final stages of refinement of both K and Cs structures the difference Fourier maps showed presence of electron density in the almost empty Fe sites on the level of 1-2 electrons. When placing Fe atom in this site with all occupation factors including factors of K or Cs refined independently, the resulting composition satisfied charge balance very accurately (within one standard deviation). Thus the general formula could be written as \(A_x\text{Fe}_{1-x}\text{Se}_2\) (\(A = K, \text{Cs}\)) and in the final refinement the occupation of Fe and M were constrained to match this composition exactly. The final R-factor was 1.9 %, 3.38 %, and 3.02 % for \(K_{0.774(6)}\text{Fe}_{1.613(2)}\text{Se}_2\), \(K_{0.738(6)}\text{Fe}_{1.631(8)}\text{Se}_2\) and \(Cs_{0.748(2)}\text{Fe}_{1.626(1)}\text{Se}_2\) crystals, respectively.

A diagrammatic representation of the structure of these alkali metal iron selenides that possesses similar body centered ThCrSi\(_2\) stacking to BaFe\(_2\)As\(_2\), are compared with the primitive symmetry of anti-PbFCl structure of NaFeAs, in Figure 2. These structures have the same morphology as BaFe\(_2\)As\(_2\). However, the 5 times larger cell now has two crystallographic inequivalent positions for potassium, iron and selenium. Of these two iron positions, one Fe sites, that was unphysical and warranted more detailed investigation. Further analysis of the crystal structure in the light of other measurements, showed that the structure can be represented in the \((\sqrt{5} \times \sqrt{5} \times 1)\) cell with the lower 14/m space group, with the presence of twinning (180° rotation around 100 axis) with approximately 1:1 ratio of twin components. This structure then yields an ordered distribution of the two Fe sites, such that one is almost completely empty, whereas one is fully occupied. The relationship between the two cells is shown in Figure 1, panel b.

Figure 1 Panel (a) Single Crystal X-ray Diffraction pattern of \(K_{0.774(6)}\text{Fe}_{1.613(2)}\text{Se}_2\) showing the relationship between the original ThCr\(_2\)Si\(_2\) cell of approximate dimensions 3.9 Å and 14 Å indicated by vectors \(a_1^*\) and \(b_2^*\) (black) compared with the reduced \((\sqrt{5} \times \sqrt{5} \times 1)\) cell (red). Figure 2. These structures have the same morphology as BaFe\(_2\)As\(_2\).
amounts, whereas Fe2 has full occupancy in all refinements. A positions are partially occupied. Fe1 is occupied with very low occupancy (0.5), Fe1 (0 0.5 0.25), Fe2 (x, y, z), Se1 (0 0 z) and Se2 (x y z). Both Fe ions represents either K or Cs. Atomic positions are homogeneously distributed within the crystal. Such occupancies could, for example, arise from small domains, such as near the crystal surface, which support the occupancy of the 4d site, leaving the rest of the crystal without iron. In either case of the presence of domains or where the crystal possesses a homogeneous distribution of 4d iron, this arrangement is grossly different to that observed for non-superconducting samples.40 The two iron sites in both the K and Cs superconducting compositions. Firstly, the non-superconducting samples have different iron distribution across the two sites, metal and less iron, although both are nominal charge balanced. The superconducting samples contain significantly more alkali metal and less iron, although both are nominal charge balanced and possess Fe2+ ions. More importantly, the superconducting samples have different iron distribution across the two sites, which is in contrast to that observed for non-superconducting samples.37 Although the refinement of the 4d Fe occupancy made a notable improvement to the fit, such low levels of iron (3.2 – 7.8%) may not be a bulk effect or homogeneously distributed within the crystal. Such occupancies could, for example, arise from small domains, such as near the crystal surface, which support the occupancy of the 4d site, leaving the rest of the crystal without iron. In either case of the presence of domains or where the crystal possesses a homogeneous distribution of 4d iron, this arrangement is grossly different to that observed for non-superconducting samples.40 Two significant differences can be highlighted between the superconducting and non-superconducting compositions. Firstly, the non-superconducting samples contain significantly more alkali metal and less iron, although both are nominal charge balanced and possess Fe2+ ions. More importantly, the superconducting samples have different iron distribution across the two sites.
with almost all occupying the general $16i$ site in preference to the $4d$ site, which will create crucial differences on the resulting electronic structure.

In summary, we determine the crystal structure of two superconducting analogues of new $\text{A}_4\text{Fe}_{16-x}\text{Se}_2$ ($\text{A} = \text{K, Cs}$) system. They possess $\text{I}4/\text{m}$ symmetry with a $\sqrt{5} \times \sqrt{5} \times 1$ cell compared with the related $\text{ThCr}_2\text{Si}_2$ structure, which is created through ordered vacancies of the Fe within the Fe–Se planes, yielding the first examples of a high temperature superconductor with structural holes within the superconducting layers. The iron atoms have a strong tendency to sit on the general $16i$ positions leaving the other $4d$ sites almost completely empty, in contrast to similar composition that do no possess superconductivity. The control of the both the alkali metal and iron compositions within the structure will be crucial in establishing a phase diagram that maps the superconductivity and antiferromagnetism.

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References

1. J. Guo, S. Jin, G. Wang, S. Wang, K. Zhu, T. Zhou, M. He, and X. Chen, Physical Review B 82, 180520 (2010).
2. F. C. Hsu, et al., Proc. Natl. Acad. Sci. 105, 14262 (2008).
3. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
4. G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Physical Review Letters 100, 247002 (2008).
5. Z. A. Ren, et al., Epl 82, 57002 (2008).
6. Z. A. Ren, et al., Chinese Physics Letters 25, 2215 (2008).
7. Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, Materials Research Innovations 12, 105 (2008).
8. X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature 453, 761 (2008).
9. R. H. Liu, et al., Physical Review Letters 101, 087001 (2008).
10. M. Rotter, M. Tegel, and D. Johrendt, Physical Review Letters 101, 107006 (2008).
11. G. F. Chen, et al., Chinese Physics Letters 25, 3403 (2008).
12. Y. Qiu, et al., Phys. Rev. Lett. 101, 257002 (2008).
13. M. J. Pitcher, D. R. Parker, P. Adamson, S. J. C. Herkelrath, A. T. Boothroyd, R. M. Ibberson, M. Brunelli, and S. J. Clarke, Chemical Communications, 5918 (2008).
14. X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, Solid State Communications 148, 538 (2008).
15. T. M. McQueen, et al., Phys. Rev. B 79, 014522 (2009).
16. W. Bao, et al., Physical Review Letters 102, 247001 (2009).
17. K. W. Yeh, et al., EPL 84, 37002 (2008).
18. M. H. Fang, H. M. Pham, B. Qian, T. J. Liu, E. K. Vehstedt, Y. Liu, L. Spinu, and Z. Q. Mao, Physical Review B 78, 224503 (2008).
19. Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, App. Phys. Lett. 94, 012503 (2009).
20. B. C. Sales, A. S. Sefat, M. A. McGuire, R. Y. Jin, D. Mandrus, and Y. Mozharivskiy, Physical Review B 79, 094521 (2009).
21. P. Zajdel, P. -Y. Hsieh, E. E. Rodriguez, N. P. Butch, J. D. Magil, J. Paglioli, P. Zavalij, M. R. Suchomel, and M. A. Green, J. Am. Chem. Soc. 132, 13000 (2010).
22. E. E. Rodriguez, P. Zavalij, P. Y. Hsieh, and M. A. Green, J. Am. Chem. Soc. 132, 10006 (2010).
23. E. E. Rodriguez, C. Stock, P. -Y. Hsieh, N. Butch, J. Paglione, and M. A. Green, arXiv 1012.0590 (2010).
24. K. O. Klepp and H. Boller, Monatshefte fuer Chemie 109, 1049 (1978).
25. G. Brun, B. Gardes, J. Tedenac, A. Raymond, and M. Maurin, Mater Res Bull 14, 743 (1979).
26. R. Berger and C. Van Bruggen, J Less-Common Met 99, 113 (1984).
27. L. Hagstrom, H. Verma, S. Bjarmann, R. Wappling, and R. Berger, Journal of Solid State Chemistry 63, 401 (1986).
28. M. Fang, H. Wang, C. Dong, C. Feng, J. Chen, and H. Q. Yuan, arXiv 1012.5236 (2010).
29. B. Shen, F. Han, X. Zhu, and H.-H. Wen, arXiv 1012.5637 (2010).
30. Y. Mizuguchi, H. Takeya, Y. Kawasaki, T. Ozaki, S. Tsuda, T. Yamaguchi, and Y. Takano, arXiv 1012.4950 (2010).
31. D. M. Wang, J. B. He, T.-L. Xia, and G. F. Chen, arXiv 1101.0789 (2011).
32. A. F. Wang, et al., arXiv 1012.5525 (2010).
33. A. Krzton-Maziop, Z. Shermadini, E. Pomjakushina, V. Pomjakushin, M. Bendele, A. Amato, R. Khasanov, H. Luetkens, and K. Conder, arXiv 1012.3637 (2010).
34. J. J. Ying, et al., arXiv 1101.1234 (2011).
35. Z. Wang, et al., arXiv 1101.2059 (2011).
36. W. Bao, Q. Huang, G. F. Chen, M. A. Green, D. M. Wang, J. B. He, X. Q. Wang, and Y. Qiu, arXiv 1102.0830 (2011).
37. J. Bacsa, A. Y. Ganin, Y. Takabayashi, K. E. Christensen, K. Prassides, M. J. Rosseinsky, and J. B. Claridge, arXiv 1102.0488 (2011).
38. J. J. Ying, et al., arXiv 1012.5552 (2010).
39. W. Yu, L. Ma, J. B. He, D. M. Wang, T.-L. Xia, and G. F. Chen, arXiv 1101.1017 (2011).
40. J. Zhao, et al., Nature Materials 7, 953 (2008).
41. A. Kreyssig, et al., Physical Review B 78, 184517 (2008).
42. C. H. Lee, et al., Journal of the Physical Society of Japan 77, 083704 (2008).