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A Novel Large Moment Antiferromagnetic Order in $K_{0.8}Fe_{1.6}Se_2$ Superconductor *

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The discovery of cuprate high T_C superconductors has inspired the search for unconventional superconductors in magnetic materials. A successful recipe has been to suppress long-range order in a magnetic parent compound by doping or high pressure to drive the material towards a quantum critical point. We report an exception to this rule in the recently discovered potassium iron selenide. The superconducting composition is identified as the iron vacancy ordered $K_{0.83(2)}Fe_{1.64(1)}Se_2$ with T_C above 30 K. A novel large moment 3.31 μ_B/Fe antiferromagnetic order that conforms to the tetragonal crystal symmetry has an unprecedentedly high ordering temperature $T_N \approx 559$ K for a bulk superconductor. Staggeringly polarized electronic density of states is thus suspected, which would stimulate further investigation into superconductivity in a strong spin-exchange field under new circumstances.

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Adding to the excitement generated by the discovery of iron-based high T_C superconductors in the past two years,[1−5] a nominal $K_{0.8}Fe_2Se_2$ material has recently been reported to have T_C above 30 K.[6] Replacing K by Rb[7] or Cs[8] also yields a superconductor at a similarly high T_C. Materials of a nominally fully occupied K site with chemical formula (Tl,A)Fe_xSe_2 (A=K or Rb) are also reported as superconductors with T_C above 30 K when iron deficient composition x∼1.8.[9,10] Superlattice peaks at $(\frac{1}{5}, \frac{3}{5}, 0)$ and $(\frac{1}{4}, \frac{3}{4}, 0)$ in the notation of the tetragonal $ThCr_2Si_2$ structure have been observed in a transmission electron microscopy study of a 33 K potassium iron selenide superconductor, and they are attributed to Fe vacancy ordering.[11] However, in our single crystal x-ray diffraction study of similar superconducting samples that have been used to detect superconducting gap in ARPES study,[12] only the $(\frac{1}{5}, \frac{3}{5}, 0)$ type of superlattice peaks are present, indicating bulk Fe vacancy order at this wave vector, and the chemical composition is determined to be charge balanced with the valence close to 2+ for Fe ions.[13] Therefore the newest family of Fe superconductors turns out not to be heavily electron doped as previous nominal formulas imply.

The ARPES studies indicate that these new iron selenide superconductors are fundamentally different from previously discovered LaFeAsO (1111), $BaFe_2As_2$, LiFeAs (111) and FeSe (11) families of iron pnictide and chalcogenide superconductors, in either lacking the hole Fermi surfaces at the center of the Brillouin zone[12] or having electronic ones,[14,15] to challenge the applicability of the prevailing $s^{\pm}$ symmetry proposed for previous Fe-based superconductors.[16,17] The superconducting gap of 8–10 meV is isotropic in plane[12,14,15] and NMR investigation indicates a spin singlet for the Cooper pair.[18] These experiments put strong constraint on possible symmetry of the superconducting order parameter. More zone center phonon modes than the tetragonal $ThCr_2Si_2$ structure would allow have been observed in optical[19] and Raman scattering[20] measurements, corroborating an enlarged $\sqrt{5}\times\sqrt{5}\times1$ crystallographic unit cell.[13] However, there are conflicting reports as to the existence of long-range magnetic order in the superconducting state from μSR and NMR work.[21,22]

In this Letter, we report a neutron diffraction study on the potassium iron selenide superconductor. Bulk superconductivity of our sample has been reported in a previous resistivity and magnetic susceptibility study.[23] We grew 10 g single crystal samples in several batches of identical condition and they were ground to powder in a helium atmosphere and then sealed with He exchange gas in a vanadium can for this work. Several pieces from each batch were measured to check the consistency of the diamagnetic response below $T_C \approx 32$ K, as shown in Fig. 1. The antiferromagnetic order and Fe vacancy order are determined in a $\sqrt{5}\times\sqrt{5}\times1$ unit cell. The ordered magnetic moment of 3.31 μ_B/Fe at 11 K is the largest among all Fe pnictide and chalcogenide superconductor materials. Magnetic transition also occurs at a record high value of $T_N \approx 559$ K below an Fe vacancy order-disorder transition at $T_S \approx 578$ K. The superconducting transition has an obvious effect on the magnetic order parameter, indicating interaction between the two coexisting long-range orders. Our results put the newest structural family of Fe superconductors in

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a unique class where high T_c superconductivity and strong magnetic order coexist. The relation between these two long range orders in unconventional superconductors, which are generally viewed as competing order parameters or the magnetic one that needs to go soft towards a quantum critical point, has to be re-assessed in light of this new discovery.

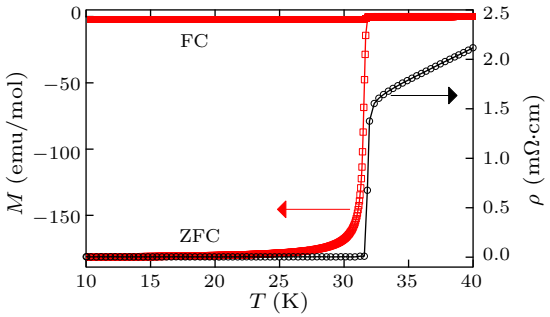

Fig. 1. Superconducting transition of the $K_{0.8}Fe_{1.6}Se_2$ sample. Magnetization measured with the sample cooled in zero magnetic field (ZFC) and in the 10 Oe measurement field (FC) is shown with resistivity.

We prefer the neutron powder diffraction method in the structure refinement to avoid complexity in the single crystal diffraction study.[13] Neutron powder diffraction patterns were measured at various temperatures from 11 to 580 K using the high resolution powder diffractometer BT1 at the NIST Center for Neutron Research (NCNR). The sample temperature below room temperature was controlled by a He closed cycle refrigerator, and above room temperature by a vacuum furnace. Cu(311) and Ge(311) monochromators were used to produce monochromatic neutron beams of wavelength 1.5403 Å and 2.0783 Å, respectively. The nuclear and magnetic structures were refined using the GSAS program.

Figure 2(b) shows the pattern at 11 K with fitting curve from the Rietveld refinement. The Fe of the starting materials was not fully reacted and was left as a 7.35(7)% impurity phase identified in the refinement. The small 2θ portion of the pattern is highlighted in Fig. 2(a). The nuclear neutron diffraction peaks from the Fe vacancy ordered crystal structure, which have been identified in our previous x-ray diffraction work,[13] are marked by a green fitting curve in the pattern at the top. The remaining neutron diffraction peaks shown below are due to antiferromagnetic long-range order. The refined crystalline and magnetic structure is presented in Fig. 3, and the refinement parameters at 11 K are listed in Table 1 together with those at other temperatures in the antiferromagnetic phase. The sample composition determined from the refinement at 11 K is $K_{0.83(2)}Fe_{1.64(1)}Se_2$. Thus, the Fe valence in this sample is very close to 2+, as in the $Fe_{1+\delta}Se$ superconductor.[24] Either the heavy electron doping or valence fluctuation, which has served as the staring point in some physics discussions on the new Fe selenide superconductors in the current literature based on incorrect nominal compositions, is misguided.

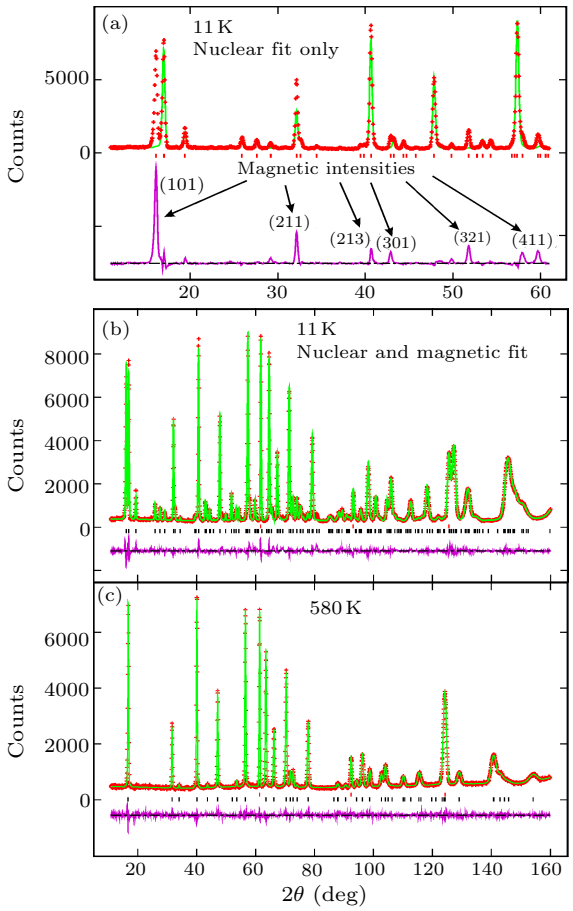

Fig. 2. Neutron powder diffraction patterns of the $K_{0.83(2)}Fe_{1.64(1)}Se_2$ superconductor. (a) Magnetic peaks are selected out of the 11 K pattern. (b) The pattern at 11 K is fitted by a Fe vacancy order described by space group $I4/m$ (No. 87) and an antiferromagnetic order by $I4/m'$ in a tetragonal unit cell of $a = b = 8.6929(2)$Å and $c = 14.0168(4)$Å. Refer to Table 1 and Fig. 3 for details. (c) The pattern at 580 K is described by the tetragonal $ThCr_2Si_2$ structure of lattice parameters $a = b = 3.94502(7)$ Å and $c = 14.1619(4)$Å. Both the Fe vacancy and the magnetic moment are disordered at high temperature. The refinement parameters are listed in Table 2.

Each unit cell of the $K_{0.83(2)}Fe_{1.64(1)}Se_2$ superconductor contains a pair of the Fe-Se layers related by inversion symmetry (see Fig. 3(a)). The top view of the Fe-Se layer is shown in Fig. 3(b). The Fe vacancy occupies the $4d$ site of the $I4/m$ space group marked by the open square. The Fe(2) site $16i$ (purple circle) is fully occupied at low temperatures. Thus, there would be no Fe site disorder in stoichiometric $K_{0.8}Fe_{1.6}Se_2$ in the Fe vacancy ordered structure, in agreement with a narrow NMR linewidth.[18,22] Each Fe(2) ion carries a saturated magnetic moment $3.31(2)\mu_B$ at 11 K, larger than the previous record of $2\mu_B$ per Fe found in the parent compounds of Fe-based superconductors.[25] The Fe magnetic moments form a collinear antiferromagnetic structure with the c-axis as the magnetic easy axis. The magnetic unit cell is the same as the

crystalline one, and the magnetic ordering vector is $\boldsymbol{Q}_m$=(101). In an important difference from all previous 1111,[26,27] 122,[28] 11[25] and 111[29] families of Fe-based superconductor materials, antiferromagnetic order in $K_{0.8}Fe_{1.6}Se_2$ occurs in a tetragonal unit cell, maintaining the four-fold crystalline symmetry. This may have important ramifications in current theoretical discussions concerning nematic order in high T_C iron superconductors.

Table 1. Refined structure parameters at 550, 500, 295 and 11 K. Space group $I4/m$ with atomic position: K1, 2*a* (0,0,0); K2, 8*h* $(x, y, 0)$, Fe1, 4*d* (0,1/2,1/4); Fe2, 16*i* (x, y, z); Se1, 4*e* $(1/2, 1/2, z)$ and Se2, 16*i* (x, y, z). A magnetic model of $I4/m'$ symmetry with only the M_z component is used in the fitting.

		550 K	500 K	295 K	11 K
	a ()	8.7853(3)	8.7785(3)	8.7308(1)	8.6929(2)
	c ()	14.1906(8)	14.1867(8)	14.1128(4)	14.0168(4)
K1	*B* (^{2})	5.9(3)	6.4(5)	3.3(2)	1.3(2)
	n	1.1(1)	1.10(7)	1.06(4)	1.04(4)
K2	*x*	0.400(4)	0.412(4)	0.403(2)	0.404(2)
	y	0.1188(4)	0.182(5)	0.180(2)	0.178(2)
	B (^{2})	5.9(3)	5.6(5)	3.3(2)	1.3(2)
	n	0.77(2)	0.76(2)	0.80(2)	0.78(2)
Fe1	*B* (^{2})	2.42(6)	2.12(7)	1.58(4)	0.58(4)
	n	0.26(1)	0.22(2)	0.059(6)	0.062(8)
Fe2	*x*	0.2012(8)	0.2019(8)	0.1984(4)	0.1979(3)
	y	0.0918(5)	0.0915(6)	0.0918(3)	0.0915(2)
	z	0.249(1)	0.2505(7)	0.2515(5)	0.2508(4)
	B (^{2})	2.42(6)	2.12(7)	1.58(4)	0.58(4)
	n	0.935(3)	0.951(4)	1.020(6)	1.008(4)
	M_z	1.22(3)	1.82(4)	3.06(2)	3.31(2)
Se1	*z*	0.145(1)	0.139(1)	0.1351(5)	0.1337(5)
	B (^{2})	2.52(6)	2.26(8)	1.02(5)	0.15(4)
	n	1	1	1	1
Se2	*x*	0.1125(8)	0.1123(9)	0.1147(4)	0.1147(4)
	y	0.296(1)	0.295(1)	0.3000(5)	0.3011(5)
	z	0.1447(3)	0.1455(3)	0.1462(2)	0.1455(1)
	B (^{2})	2.52(6)	2.26(8)	1.02(5)	0.15(4)
	n	1	1	1	1
	Rp (%)	6.17	6.75	5.15	4.99
	Rwp(%)	7.66	8.61	6.71	6.93
	χ^2	1.075	1.472	1.975	4.212

Table 2. Refined structure parameters at 580 K. Space group $I4/mmm$ with $a = 3.94502(7)$ Å and $c = 14.1619(4)$ Å.

Atom	Site	*x*	*y*	*z*	$B_{11} = B_{22}$ (^{2})	B_{33} (^{2})	n
K	2a	0	0	0	6.4(2)	6.1(5)	0.86(1)
Fe	4d	0	1/2	1/4	2.725(5)	3.2(1)	0.805(4)
Se	4e	0	0	0.35444(9)	3.01(5)	3.8(1)	1

$Rp = 3.88\%$, $Rwp = 4.22\%$, and $\chi^2 = 1.379$.

Being commensurate with the crystal structure, the antiferromagnetic order in $K_{0.8}Fe_{1.6}Se_2$ is not as complex as the incommensurate one in $Fe_{1+\delta}Te$ ($\delta > 0.14$),[25] but it is considerably more complex than the two kinds of commensurate antiferromagnetic in-plane orders observed so far in iron pnictide and chalcogenide parent compounds, for which magnetic moments are parallel to each other along the shorter *b*-axis.[25,26,28,29] A convenient way to comprehend the antiferromagnetic structure of $K_{0.8}Fe_{1.6}Se_2$ is to consider the four parallel magnetic moments at the center or the corners of the unit cell as a supermoment (see Fig. 3(b)). The supermoments then form a simple checker-board nearest-neighbor antiferromagnetic order on a super square lattice. It is interesting to note that along the edge of the primitive Fe square lattice, the sign of a string of four Fe(2) moments, terminated by the empty Fe(1) site, follows the same $+ - -+(- + +-)$ pattern as found in the commensurate antiferromagnetic order in $Fe_{1+\delta}Te$ ($\delta \leq 0.076$).[25] This observation suggests similar magnetic interaction in the *ab*-plane as in the 11 antiferromagnets. Along the *c*-axis, antiferromagnetic coupling prevails in $K_{0.8}Fe_{1.6}Se_2$ as well as in LaFeAsO,[27] 122,[28] 11[25] and 111[29] antiferromagnetic compounds, unless the rare earth magnetic ordering alters the coupling to become a ferromagnetic one in the 1111 compounds.[26] It would be interesting to investigate how our observed antiferromagnetic order is stabilized over those proposed in theoretical study.[30]

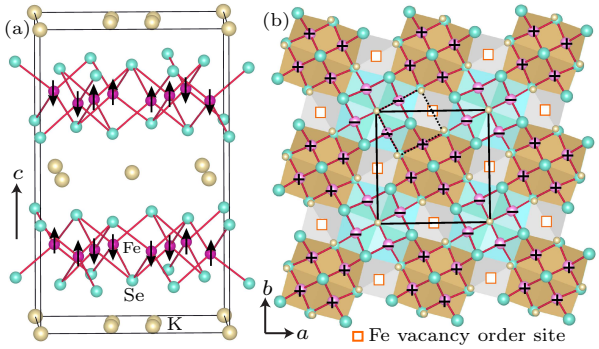

Fig. 3. Crystal and magnetic structure of $K_{0.8}Fe_{1.6}Se_2$ in the low-temperature $I4/m$ unit cell. (a) The top and bottom Fe-Se layers, including magnetic moment orientation, form a mirror image of each other by the horizontal plane at $c/2$. (b) Top view of the top Fe-Se layer. The black solid line marks the $I4/m$ unit cell. The iron vacancy site Fe(1) is marked by the open square, and the fully occupied Fe(2) site by the purple circle with the + or − sign indicating magnetic moment direction that has only the *c*-axis component. The high-temperature $I4/mmm$ unit cell is marked by the dashed line, for which the low-temperature $I4/m$ unit cell is a $\sqrt{5}\times\sqrt{5}\times1$ supercell. There are two equivalent ways to generate from the high-temperature unit cell and the low-temperature supercell with different "handedness". Both of the handedness twins exist with equal probability in our sample according to our single crystal diffraction study.

The most surprising aspect of the large moment antiferromagnetic order in $K_{0.83(2)}Fe_{1.64(1)}Se_2$ is its coexistence with the high $T_C \approx 32$ K superconductivity. Figure 4 presents a magnetic Bragg peak (101) as a function of temperature. The Néel temperature $T_N \approx 559$ K is astonishingly high for a superconductor, corroborating a recent report of a lower yet very high $T_N \approx 477$ K in a closely related superconductor of nominal composition $Cs_{0.8}Fe_2Se_{1.96}$ from a μSR study.[21] In a wide temperature range below ~500 K,

the squared magnetic order parameter increases linearly with decreasing temperature (Fig. 4). However, it departs from the trend at 40 K when T_C is approached. The anticipation of the incipient superconducting transition indicates interaction between magnetism and superconductivity as previously found for heavy fermion superconductors.[31]

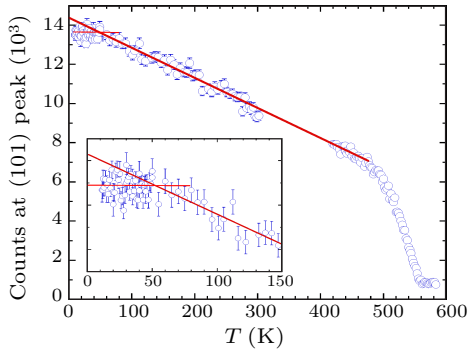

Fig. 4. The magnetic Bragg peak (101) appears below the Néel temperature $T_N \approx 559$ K. Below ∼500 K, the Bragg intensity increases linearly with decreasing temperature, then turns to be flat below ∼40 K. The inset highlights the low-temperature part.

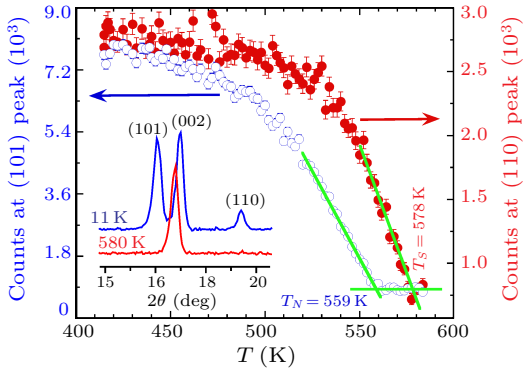

Fig. 5. Magnetic order depends on Fe occupancy order. The magnetic Bragg peak (101) and structural peak (110) as a function of temperature, showing magnetic transition at $T_N = 559$ K and structural transition at $T_S = 578$ K. Inset: powder diffraction patterns at 11 and 580 K. The (002) exists in both the $I4/mmm$ and $I4/m$ phases. The appearance of (110) signifies the reduction in the $I4/mmm$ crystalline symmetry to the $I4/m$. The (101) develops with the antiferromagnetic order on the sublattice of Fe(2) ions.

The order-disorder transition of the Fe vacancy occurs at $T_S \approx 578$ K, about 20 K above T_N, as shown in Fig. 5. Unlike the magnetic (101) peak, the structural Bragg peak (110) due to Fe vacancy order saturates towards its low temperature value rapidly. At room temperature, there is little difference in the (110) intensity, henceforth in the vacancy order, from that at 11 K (see Table 1). The disappearance of the (110) peak above T_S signifies the equivalence of the Fe(1) and Fe(2) sites and the restoration of the $I4/mmm$ symmetry of the $ThCr_2Si_2$ structure. The neutron powder diffraction pattern at 580 K shown in Fig. 2(c) is fitted using the parameters listed in Table 2. The iron site is 80.5(4)% occupied. A lower T_N than T_S in $K_{0.8}Fe_{1.6}Se_2$ confirms our expectation that the establishment of the antiferromagnetic order depends on the development of the Fe occupancy order.

In summary, the bulk superconductor $K_{0.83(2)}Fe_{1.64(1)}Se_2$ is almost charge balanced. The condensation of the Fe^{2+} ions onto the Fe(2) site at $T_S \approx 578$ K leads to a well ordered almost stoichiometric crystal structure in $I4/m$ symmetry. A novel antiferromagnetic order with large saturated moment $3.31(2)\mu_B$ per Fe develops on the vacancy decorated lattice below $T_N \approx 559$ K. Remarkably, superconductivity at a high $T_C \approx 32$ K realizes in such a strong magnetic environment. Since the new iron selenide superconductors are of a completely different structure, even if signatures of unconventional superconductivity of the $s^{\pm}$ symmetry do not materialize in the new iron selenide superconductors, it may not lead to automatic disqualification of the theory for the former families of the iron-based 1111, 122, 111 and 11 superconductors.

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