Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Iron vacancy in tetragonal $Fe_{1-x}S$ crystals and its effect on structure and superconductivity

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Preparation of $K_{0.8}Fe_{1.6}S_2$ single crystals

The single crystals of $K_{0.8}Fe_{1.6}S_2$ (245 phase) were grown via self-flux method with the nominal composition K : Fe : S = 0.8 : 1.6 : 2. The pressed FeS disc and K pieces were added into the alumina crucible, inside a quartz tube. The quartz tube was sealed under vacuum, heated at 1040 °C for 15 hours and then slowly cooled down to 800 °C, followed by furnace cooling to the room temperature.

Table S1. The detailed mass of the raw materials of five samples and the yield of the $Fe_{1-x}S$ products.

No.	245	NaOH	Thiourea	Fe	$Fe_{1-x}S$	*x* from	*x* from	*x* from	R_{Fe}[&]	R_S[&]
	(g)	(g)	(g)	(g)	(g)	ICP-MS	EDS[*]	ICSA		
#1	0.2405	0.12	0.2283	0.16	0.1832	-0.013(10)	0.013 (6)	-0.01(1)	1.023	0.818
#2	0.2410	0.12	0.2284	0.12	0.1837	0.01(1)	0.01(1)	0.00(1)	1.067	0.854
#3	0.2403	0.12	0.2286	0.08	0.1867	0.054(10)	0.067(9)	0.05(1)	0.987	0.831
#4	0.2408	0.12	0.2289	0.04	0.1901	0.081(8)	0.090(8)	0.105(10)	0.927	0.815
#5	0.2407	0.12	0.2281	0	0.1909	0.094(8)	0.10(1)	0.11(1)	0.936	0.832

***** The chemical composition from EDS was the average value for measuring 7-10 areas on each sample surface (around 30 μm^2).

[&] The R_{Fe} and R_S represent the ratio of the Fe and S mass between $Fe_{1-x}S$ crystals and that in 245 precursors.

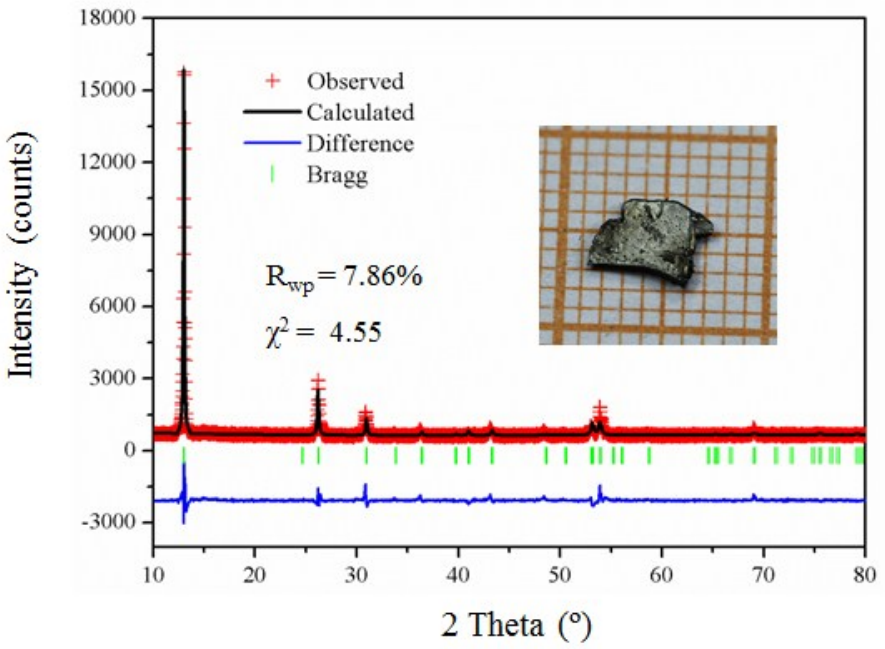

Fig. S1 PXRD pattern and Rietveld refinement of $K_{0.8}Fe_{1.6}S_2$. The inset shows the optical photograph of the crystal sample.

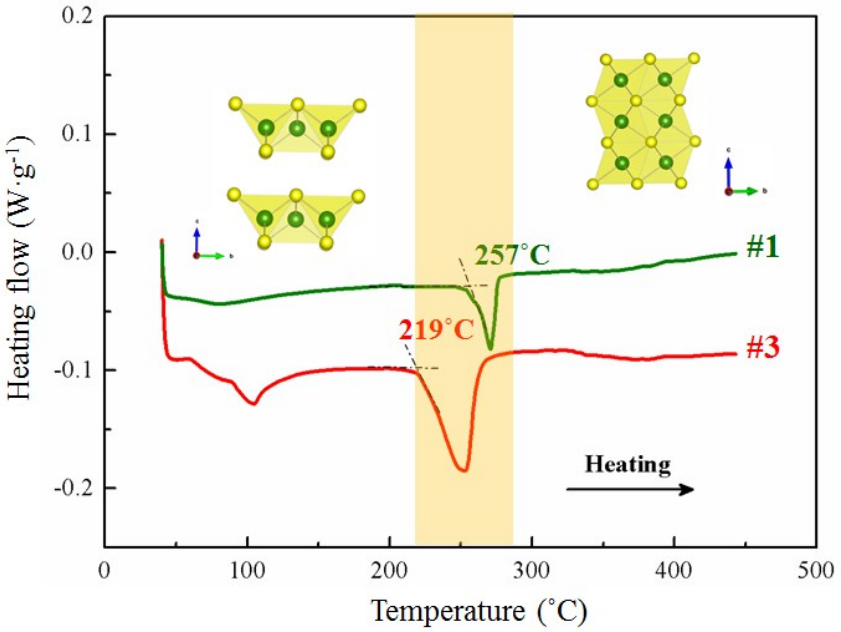

Fig. S2 DSC heating curves of the sample #1 and #3, showing the decomposition temperature as 257 and 219 ˚C, respectively. According to the literature,[1] the tetragonal $Fe_{1-x}S$ would transform to the hexagonal pyrrhotite at higher temperature (Inset).

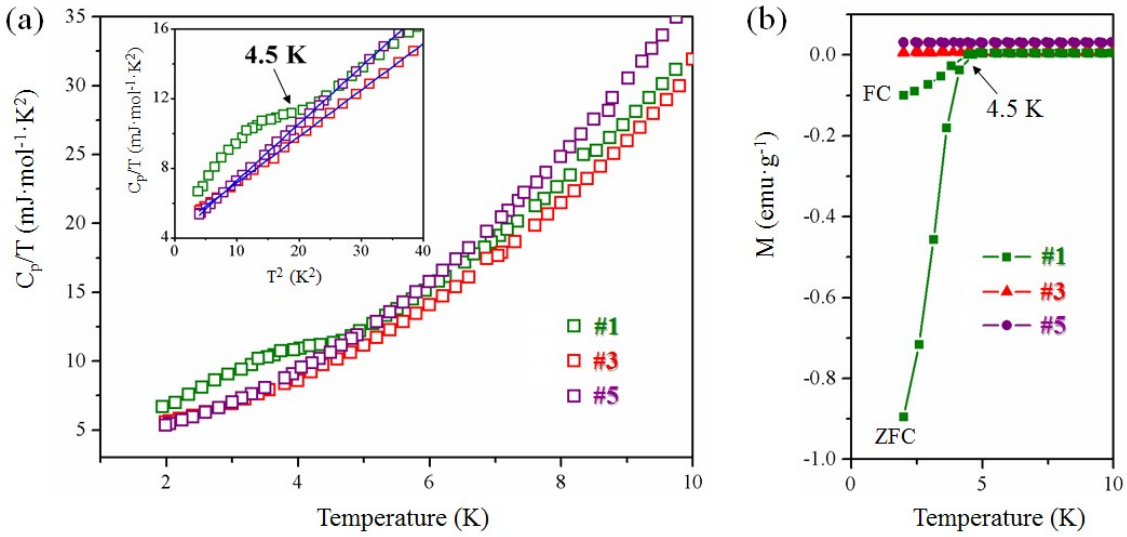

Fig. S3 (a) Temperature dependence of specific heat from 2 to 10 K with the field of 0 T. Inset shows the plots of C_p/T versus T^2 to fit the electron and phonon model: $C_p = \gamma T + \beta T^3$, where γ is Sommerfield coefficient and β is phonon term. (b) Temperature dependence of magnetic susceptibility from 2 to 10 K in both zero-field cooling (ZFC) and field cooling (FC) modes at 20 Oe with the field parallel to *c* axis of the samples. Both these two measurements indicate the *SC* in sample #1 with T_c = 4.5 K, while sample #3 and #5 are non-*SC*.

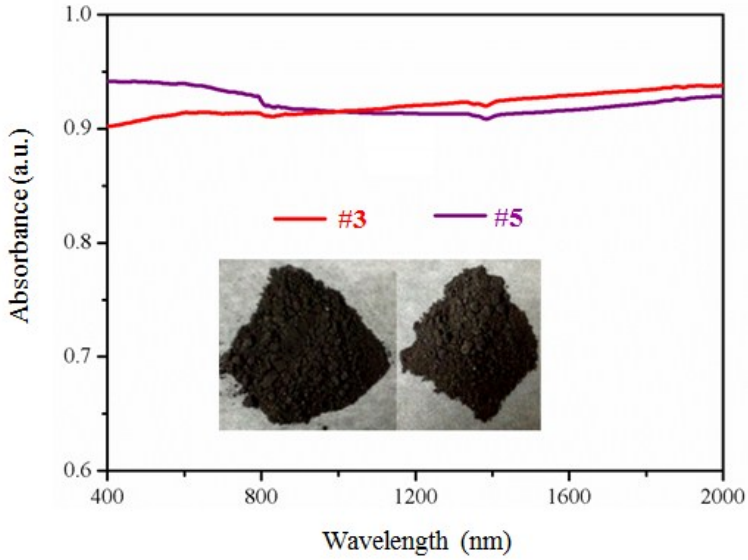

Fig. S4 UV−vis−NIR diffuse-reflectance spectra of semiconducting #3 and #5 powder samples (from the grinded crystals), where no band gap has been observed due 2000 nm (which means that the band gap should be narrower than 0.62 eV). Inset shows the optical photograph of sample #3 and #5, both showing black color after grind.

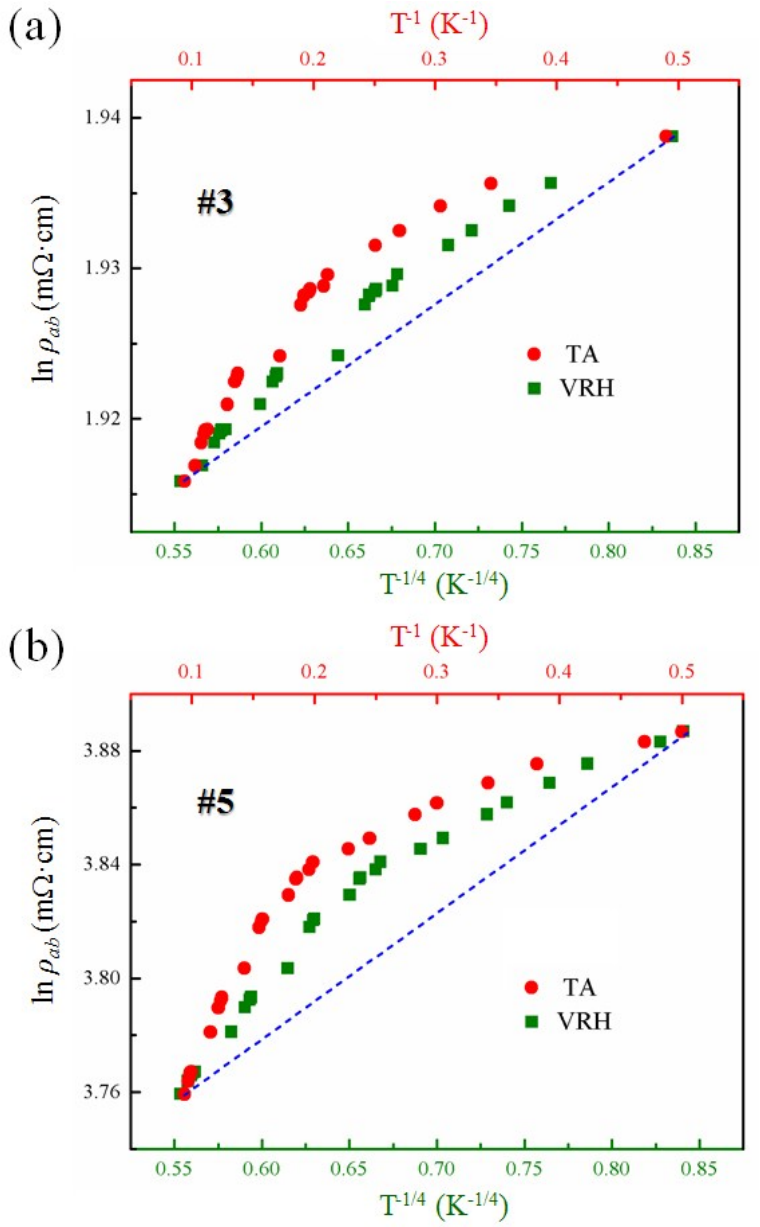

Fig. S5 Sample #3 and #5: The plots of lnρ/T versus T^{-1} and lnρ versus $T^{-1/4}$ to fit thermal activation model (*TA*) and variable range hopping model (*VRH*) with the data in the low temperature range (from 2 to 10 K). The blue dash line highlights that both T^{-1} and $T^{-1/4}$ are out of the linear dependence on lnρ_{ab}.

Table S2. The Rietveld refinement parameters of five samples, #1, #2, #3, #4 and #5.

No.	#1	#2	#3	#4	#5
Formula from refinements	FeS	FeS	$Fe_{0.96}S$	$Fe_{0.93}S$	$Fe_{0.92}S$
Space Group			*P*4/*nmm*		
a(Å)	3.6805(3)	3.6806(4)	3.6768(4)	3.6735(6)	3.6726(4)
c(Å)	5.0294(4)	5.0292(7)	5.0318(7)	5.0367(9)	5.0374(7)
V(Å^3)	204.812	202.091	202.091	192.895	187.186
Fe			0.75, 0.25, 0		
S	0.25, 0.25, 0.2539(2)	0.25, 0.25, 0.2547(2)	0.25, 0.25, 0.2601(2)	0.25, 0.25, 0.2574(3)	0.25, 0.25, 0.2587(2)
R_{wp}	2.32%	3.09%	2.27%	3.54%	2.27%
χ^2	1.75	2.62	2.01	1.32	1.64

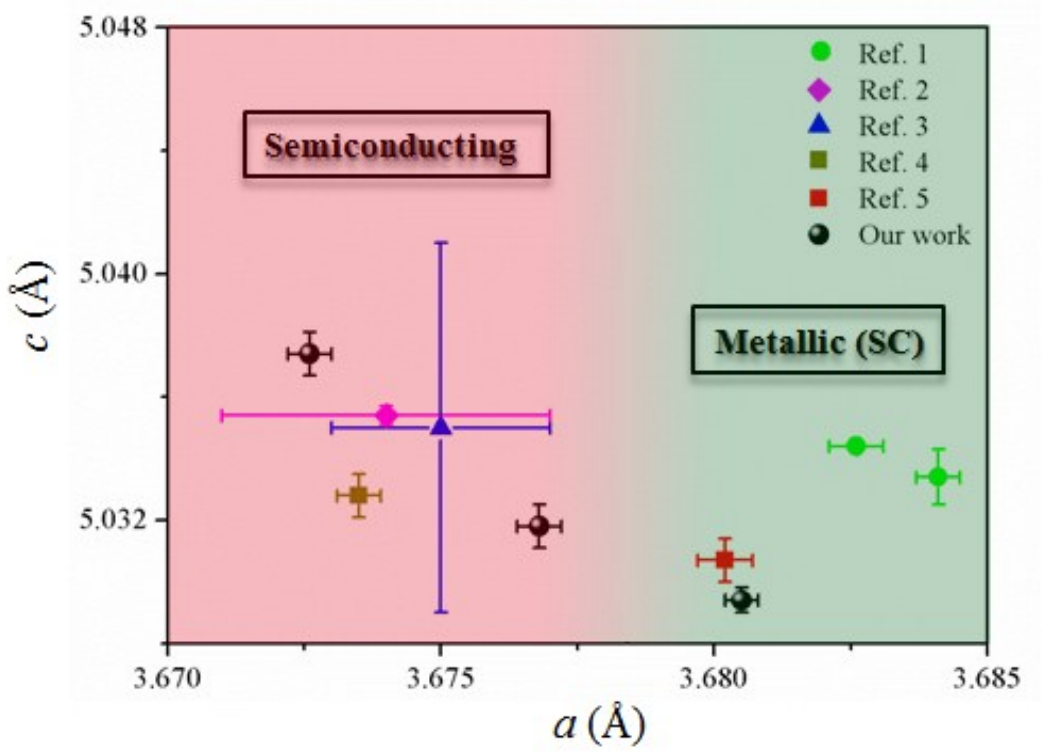

Fig. S6 Lattice parameters obtained from the literature[1-5] and our work, showing that all the samples showing metallic state with *SC* have the parameter *a* larger than 3.68 Å, while the ones with *a* smaller than 3.677 Å show semiconducting behavior without *SC*. The only exception was reported by Zeng et al, who synthesized tetragonal FeS by reacting Fe powder and sulfide solution, and obtained the semiconducting sample with a quite large parameter $a = 0.3767(1)$ Å.[6]

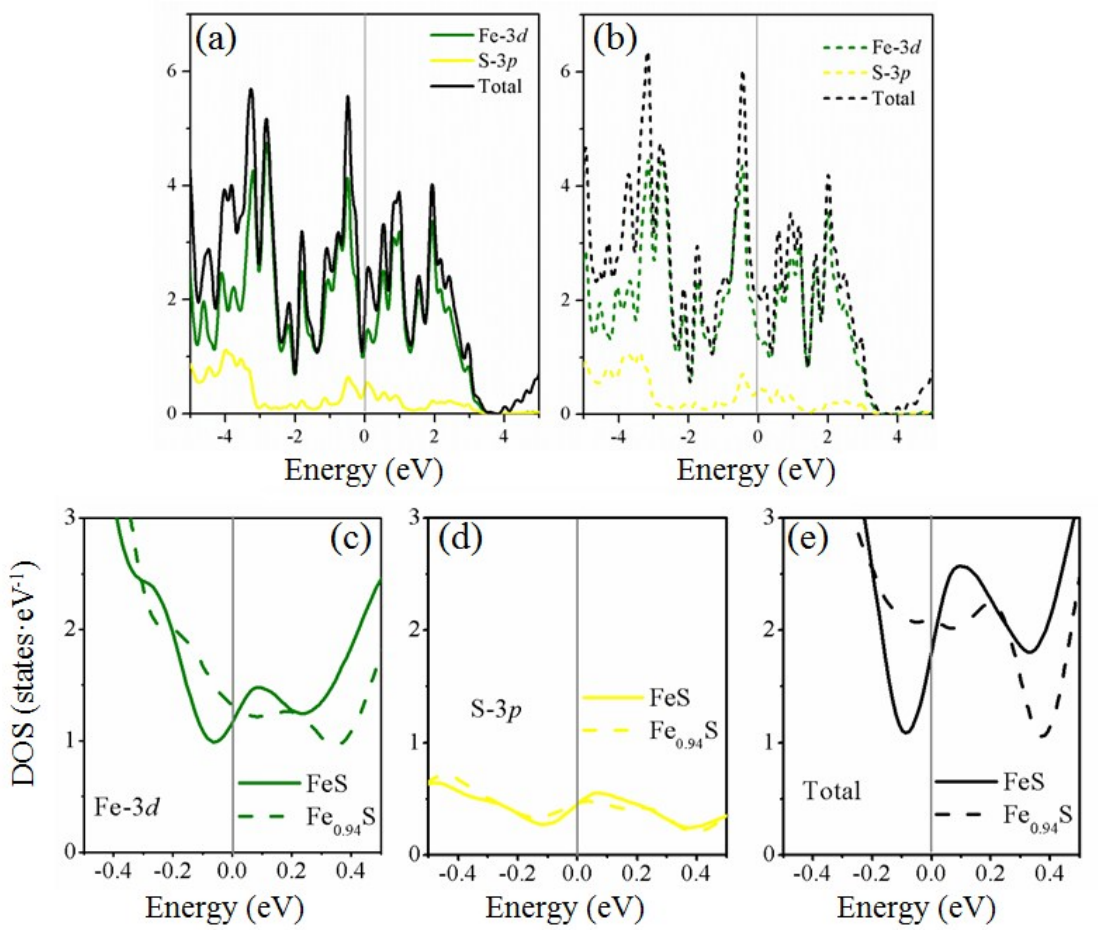

Fig. S7 The total and partial DOS of (a) vacancy free FeS and (b) $Fe_{0.94}S$. The partial enlarged detail near the Fermi level of Fe-3*d*, S-3*p* and total quantity are given in (c), (d) and (e), where the vacancy slightly increased the DOS at the Fermi level contributed from the Fe-3*d* orbitals.

References

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