Superconducting Order from Local Disorder

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Abstract: In all Fe superconductors the maximal $T_c$ correlates with the average anion height above the Fe plane, i.e. with the geometry of the FeAs$_4$ or FeCh$_4$ (Ch=Te,Se,S) tetrahedron. By synthesizing FeSe$_{1-x}$S$_x$ (0 $\leq$ x $\leq$ 1) single crystals we find that $T_c$ does scale with the average anion height for x in the presence of nematic order and near FeS, whereas superconductivity changes for all other x track local crystallographic disorder and disorder-related scattering. Our findings demonstrate the strong coupling between disorder and $T_c$ as x is tuned beyond the nematic critical point (NCP) and provide evidence of a $T_c$ tuning related to local crystal parameters.

Main Text: The connection between superconducting ($T_c$) and nematic ($T_s$) order with crystalline disorder is crucial, yet poorly understood in Fe and Cu-based high-$T_c$ superconductors alike [1-4]. In Fe-based superconductors the maximal $T_c$ correlates with the average anion height above the Fe plane; the height depends on the geometry of the FeAs$_4$ or FeCh$_4$ (Ch=Te, Se, S) tetrahedron. The geometry also regulates the correlation strength due to the average Fe-As(Ch) hybridization, pointing to a spin fluctuation pairing mechanism [5-6].

A dome-like magnetic phase supersedes the nematic order in pressurized FeSe and $T_c$ = 37 K is obtained at 6 GPa; in contrast no magnetic order was found and only weak changes in the $T_c$ were detected in FeSe$_{1-x}$S$_x$ (0 $\leq$ x $\leq$ 0.2) [7-9]. An abrupt change of the superconducting gap structure points to two distinct pairing states as S substitutes Se across the NCP around x=0.2 [10-12]. Sulfur substitution in FeSe could simply suppress electronic correlations associated with Fe $d_{xy}$ orbitals [13]. Consequently, one should expect a smooth change of $T_c$ between FeSe (~ 10 K) to FeS (~ 5 K).
Due to the complex Fe-Se/S composition-temperature phase diagram and the unstable tetragonal phase the complete evolution of $T_c$ in FeSe$_{1-x}$S$_x$ ($0 \leq x \leq 1$) and underlying crystallographic parameters are still unknown. However, in contrast to the complex copper oxides, the simpler crystal chemistry might allow for deeper insight into the disorder-induced connection between the material crystallography and properties of interest. To address this challenge, we present the entire progression of superconducting $T_c$ and crystallographic changes from FeSe to FeS.

The resistivity anomaly associated with the structural transition at $T_s$ in FeSe is suppressed to lower temperature by S [Fig. 1(a, b)] approaching $T \rightarrow 0$ K above $x = 0.18$ [10]. The $T_c$ increases slightly with S doping from 9.3 K in FeSe to 10.9 K in FeSe$_{0.8}$S$_{0.10}$ [14] whereas the transition width becomes broader and $T_c$ decreases quickly with further doping, reaching a minimum value of 2.1 K at $x = 0.4$. With even higher sulfur substitution $T_c$ increases slowly up to 4.6 K for $x = 1$. The $T_c$ values are consistent with the ones inferred from magnetic susceptibility [15].

To estimate the disorder-related scattering, we consider \( \rho(300K)/\rho(14K) \) as residual resistivity ratio (RRR) for all $x$ [Fig. 1(c)]. In general, smaller values denote larger disorder-related scattering strength. There is a continuous decrease of RRR from $x = 0$ to $x = 0.16$ in FeSe as S atoms substitute Se and as the structural transition is suppressed. When the structural/nematic transition is completely suppressed, the RRR increases to about 25. The RRR decreases with further increase in $x$ and $T_c$ increases up to $x = 0.4$, steeply rising to 54 at $x = 1$. The RRR changes with $x$ are also reflected in the residual resistivity values in the normal state close to $T_c$, $\rho_{14K}$.

We analyze the normal-state transport properties in the about 30 K range above $T_c$ using $\rho(T) = \rho_0 + AT^\alpha$, where $A$ and the power $\alpha$ are constants that describe the electronic transport and its deviation from the $\alpha = 2$ expected for a Fermi liquid [16]. Fit results are presented in Fig.1(d): $\alpha$ decreases from 1.2 in FeSe as $T_s$ approaches $T_c$ with doping down to 0.34 at $x = 0.16$. The exponent $\alpha$ recovers to 1.2 when the structural transition is fully suppressed and increases to 2 as $x$ changes from $x = 0.8$ to $x = 1$, i.e. for FeS. This shows the crossover from non-Fermi- to Fermi-liquid transport with increasing $x$ [12]. Next, we focus on crystallographic details across the phase diagram.

The evolution of the unit cell parameters with Si, inferred from the Rietveld refinement of the average crystal structure [Fig. 2(a)] shows that both the $a$ and $c$ lattice parameters decrease monotonically with $x$. However, $a$ and $c$ evolve at a different rate at low doping, in contrast to same rate at the higher doping level. This change manifests itself as a clear kink in the $c/a$ ratio [Fig.2(b)] near $x = 0.4$. The simultaneous decrease of the $c/a$ ratio and the suppression of the resistivity hump with increasing $x$ [Fig. 1(a, b)] suggest a crossover from incoherent at elevated temperature to coherent conduction as the average crystal structure becomes more three-dimensional. The reduction of the $c/a$ ratio is stronger in the S-substituted samples than in pure FeSe under high pressure where the crystal structure of the superconducting phase having maximal $T_c$ at 37 K changes, and magnetic order is observed up to 40 GPa [7,8]. The absence of long-range magnetic order can be explained by the collapse of the effect of chemical pressure just before the critical pressure for magnetic order is reached, as indicated by the sharp deviation from the initial slope of the $c/a$ ratio near the NCP [Fig. 2(b)] [15].

To shed light on the chemical bonding and the key parameters of the local crystallography of FeCh$_{4}$ (Ch=Se,S) tetrahedra we studied the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine-structure (EXAFS) which provide information on the hybridization between the Fe 3d and Ch 4p orbitals as well as accurate Fe-Ch bond distances. The typical Fe K-edge $A$, $B$, $C$ and the Se K-edge $D$, $E$ XANES features [Fig. 2 (c, d)] point to increased $d$–$p$ hybridization with $x$, expected to promote delocalization [15]. The Fourier transform (FT) magnitudes of the EXAFS oscillations weighted by $k^2$ and extracted from the Fe K and Se K-edges [Fig. 2(e, f)] indicate different values of the Fe-Se and Fe-S bond lengths [Fig. 2(g, h)] [15]. The Fe-Se bond length shows a weak increase for $x \leq 0.10$, along with that of $T_c$ [Fig. 1(a, b)] and a decrease for further S substitution results as $x \rightarrow 1$. Different Fe-S and Fe-Se bonds illustrate rather deformed FeCh$_4$
tetrahedra. Consequently, there is a local structure inhomogeneity in the middle of the alloy series due to the comparable numbers of Fe-Se and Fe-S bonds in FeCh₄ [15].

In Fe-based superconductors the highest $T_c$ values are observed for regular Fe-Ch(As) tetrahedrons, empirically scaling with the average Ch(As) height above the Fe plane [5]. We plot the average anion height from Rietveld refinement in Fig. 3(a). Note that the concept of anion height comes from the average crystal structure; it does not contain information from local crystallography such as distinct Fe-S and Fe-Se bond length distances. The $T_c$ does scale with Fe height near FeSe and for FeS, showing only small deviations in the nematic and in the Fermi liquid region of the phase diagram.

For all other x, changes in the resistivity ratio $RRR(x)$ relative to that of FeSe [$RRR(x)/RRR(FeSe)$], being a direct probe of relative crystallographic disorder-related scattering [17,18], trace closely $T_c$ except at NCP around $x = 0.2$ [Fig. 3(a)]. In the nematic part of the phase diagram $T_c$ shows an increase even though disorder-related scattering is increased. Near FeS, as opposed to FeSe, the increase in $RRR(x)$ does not result in a higher $T_c$.

We also note that the evolution of the superconducting $T_c$ with x is tracked by the disorder in the Bragg plane distances along the c-axis for all x except at NCP, as shown by the full width at half maximum (FWHM) of diffraction peaks taken on single crystals normalized to the FWHM of pure FeSe ($x = 0$) [15]. For clarity and for easier comparison with the RRR and $T_c$ changes, we plot the normalized [FWHM(x)]$^{-1}$; smaller values denote higher relative disorder in the c-axis Bragg plane when compared to FeSe.

The FeSe$_{1-x}$S$_x$ phase diagram up to the NCP [Fig. 3(a)] points to nematic interactions-driven Cooper pairing [2] since the weak increase in $T_c$ coincides with melting of the nematic order, and the maximal $T_c$ occurs for $x$ values near the sharp drop of $T_s$. The insensitivity of $T_c$ to disorder or even its mild increase for small S doping is not expected for a phonon mechanism of Cooper pairing in either FeSe or FeS [3,19,20]; however it is consistent with the orbital-selective spin fluctuation scenario with atomic-scale disorder and inhomogeneous pairing interactions which could enhance $T_c$ [4,21].

To explore this further, we venture beyond the NCP as x is increased towards the middle of the phase diagram where the impact of disorder strength is not weak, and where Fe-Ch tetrahedra feature the highest bond disorder [Fig. 2(g, h)] since S substitutes Se in a random-alloy manner [15]. Angular resolved photoemission spectroscopy (ARPES) near the Γ point in the Brillouen zone [Fig. 3(b)] for FeSe$_{0.97}$S$_{0.03}$ is consistent with the previous result [22,23]. As x is increased, the electronic structure shows a significant reconstruction for $x = 0.9$ [Fig. 3(c)], as shown by the binding energy change observed in the clearly resolvable ε band. This indicates that the RRR increase at $x = 0.9$ [Fig. 1(a)] is directly tied to the higher conductivity of pure FeS originating from the bandwidth increase because of weaker correlations [6,22], unrelated to disorder. Moreover, there is a considerable change [Fig. 3(d-f)] in the Fermi surface near the Γ point as seen in the electronic scattering rate $1/\tau$ as $x$ is tuned from the nematic ($x = 0.1$) to the overdoped region ($x = 0.7$) [star symbols in Fig. 3(a)]. The trend of change shows good agreement with $T_c(x)$. Larger scattering rates are found in samples with smaller RRR and larger $c$-axis Bragg plane disorder. Observed changes in $(1/\tau)(x)$ are much larger when compared to scattering rates due to electronic correlations variation with x calculated within DFT+DMFT framework [11,15].

The Raman active A$_{1g}$ and B$_{1g}$ phonon modes correspond to fully symmetric and the out-of-phase local vibration of the chalcogen and Fe atoms along the c-axis, respectively [25-27]. The B$_{1g}$ mode has the same symmetry as the nematic fluctuations, both charge and spin, and is therefore expected to couple to deformations of this type [26,28,29]. Both lines broaden due to disorder [Fig. 3(a)] as x is increased [15]. However, whereas the inverse half-width of the B$_{1g}$ phonon [FWHM B$_{1g}(x)$]$^{-1}$ tracs $T_s(x)$, [FWHM A$_{1g}(x)$]$^{-1}$ does not. A picture emerges where variation of the crystallographic disorder with x induces spin fluctuations that affect the electronic carrier scattering rates $(1/\tau)$ near the Γ point.
In metals, scattering rate \(1/\tau = (1/\tau_e + 1/\tau_i)\) represents the sum of elastic \(1/\tau_e\) and inelastic components \(1/\tau_i\). Impurities and crystallographic defects/disorder commonly contribute to elastic scattering. Since the Fe-S and Fe-Se bond lengths retain the FeSe and FeS values for all \(x\), the Fe-Ch (Ch = Se, S) bond length [Fig. 2(h)] [15] and \(c\)-axis Bragg plane disorder are high in the middle of the phase diagram. This may also give rise to inelastic scattering due to charge-nematic or magnetic spin fluctuations because the bond lengths regulate the Fe-Ch overlap and the FeCh₄ tetrahedron shape which, in turn, controls the crystal field levels and thus the orbital occupancies and relative mixing of Fe \(d_{xz}\) and \(d_{yz}\) [2, 6, 21, 26, 29]. The absence of a nematic transition for \(x\) beyond the NCP points to smearing of the \(d_{xz}\) and \(d_{yz}\) splitting due to a combination of disorder and a reduction of the spin-orbit coupling as S substitutes Se [30]. \(T_c(x)\) shadows disorder changes since, within the concept of orbital-selective Cooper pairing, the pairing strength is related to the orbital-selective correlations and well-defined quasiparticle weights of the Fe \(d_{yz}\) and \(d_{xz}\) orbitals at the Fermi surface [3,31-33]. We expect that our finding will stimulate further experiments and theoretical methods to connect superconductivity with local crystallographic disorder in materials with nematic fluctuations.

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**References and Notes:**

[1] L. Nie, G. Tarjus, and S. A. Kivelson, *Proc. Natl. Ac. Sci.*, **111**, 7980 (2015).

[2] R. M. Fernandes, A. V. Chubukov, and J. Schmallian, What drives nematic order in iron-based superconductors? *Nature Physics* **10**, 97 (2014).

[3] P. O. Sprau, A. Kostin, A. Kreisel, A. E. Böhm, V. Taufour, P. C. Canfield, S. Mukherjee, P. J. Hirschfeld, B. M. Andersen and J. C. Séamus Davis, *Science* **357**, 75 (2017).

[4] L. Benfatto, B. Valenzuela and L. Fanfarillo, *NPJ Quantum Materials* **3**, 56 (2018).

[5] Y. Mizuguchi, Y. Hara, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou, and Y. Takano, *Supercond. Sci. Technol.* **23**, 054013 (2010).
[6] Z. P. Yin, K. Haule and G. K. Kotliar, *Nature Mater.* 10, 932 (2011).
[7] S. Medvedev, T. M. McQueen, I. A. Troyan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann and C. Felser, *Nature Mater.* 8, 630 (2009).
[8] J. P. Sun, K. Matsuura, G. Z. Ye, Y. Mizukami, M. Shimozawa, K. Matsubayashi, M. Yamashita, T. Watashige, S. Kasahara, Y. Matsuda, J.-Q. Yan, B. C. Sales, Y. Uwatoko, J.-G. Cheng, and T. Shibauchi, *Nat. Commun.* 7, 12146 (2016).
[9] Y. Sato, Shigeru Kasahara, Tomoya Taniguchi, Xiangzhuo Xing, Yuichi Kasahara, Yoshifumi Tokiwa, Youichi Yamakawa, Hiroshi Kontani, Takasada Shibauchi, and Yuji Matsuda, *Proc. Natl. Acad. Sci.* 115, 1227 (2018).
[10] S. Hosoi, K. Matsuura, K. Ishida, H. Wang, Y. Mizukami, T. Watashige, S. Kasahara, Y. Matsuda, and T. Shibauchi, *Proc. Natl. Acad. Sci.* 113, 8139 (2016).
[11] A. I. Coldea, Samuel F. Blake, Shigeru Kasahara, Amir A. Haghighirad, Matthew D. Watson, William Knafo, Eun Sang Choi, Alix McCollam, Pascal Reiss, Takuya Yamashita, Mara Bruma, Susannah C. Speller, Yuji Matsuda, Thomas Wolf, Takasada Shibauchi and Andrew J. Schofield, *NPJ Quantum Materials* 4, eaar6419 (2018).
[12] S. Licciardello, J. Buhot, J. Lu, J. Ayres, S. Kasahara, Y. Matsuda, T. Shibauchi and N. E. Hussey, *Nature* 567, 213 (2019).
[13] P. Reiss, M. D. Watson, T. K. Kim, A. A. Haghighirad, D. N. Woodruff, M. Bruma, S. J. Clarke, and A. I. Coldea, *Phys. Rev. B* 96, 121103(R) (2017).
[14] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, *J. Phys. Soc. Jpn.* 78, 074712 (2009).

[15] Supplementary Material.
[16] A. Rosch, *Phys. Rev. Lett.* 82, 4280 (1999).
[17] A. E. Böhmer, V. Taufour, W. E. Straszheim, T. Wolf, and P. C. Canfield, *Phys. Rev. B* 94, 024526 (2016).
[18] S. Rössler, Chien-Lung Huang, Lin Jiao, Cevriye Koz, Ulrich Schwarz, and Steffen Wirth, *Phys. Rev. B* 97, 094503 (2018).
[19] C.-L. Song, Yi-Lin Wang, Peng Cheng, Ye-Ping Jiang, Wei Li, Tong Zhang, Zhi Li, Ke He, Lili Wang, Jin-Feng Jia, Hsiang-Hsuan Hung, Congjun Wu, Xucun Ma, Xi Chen and Qi-Kun Xue, *Science* 332, 1410 (2011).
[20] X. Yang, Zengyi Du, Guan Du, Qiangqiang Gu, Hai Lin, Delong Fang, Huan Yang, Xiyu Zhu and Hai-Hu Wen, *Phys. Rev. B* 94, 024521 (2016).
[21] A. T. Römer, P. Hirschfeld and B. M. Anderson, *Phys. Rev. Lett.* 121, 027002 (2018).
[22] J. Miao, X. H. Niu, D. F. Xu, Q. Yao, Q. Y. Chen, T. P. Ying, S. Y. Li, Y. F. Fang, J. C. Zhang, S. Ideta, K. Tanaka, B. P. Xie, D. L. Feng, and F. Chen, *Phys. Rev. B* 95, 205127 (2017).
[23] M. D. Watson, T. K. Kim, A. A. Haghighirad, S. F. Blake, N. R. Davies, M. Hoesch, T. Wolf and A. I. Coldea, *Phys. Rev. B* 92, 121108 (2015).
[24] M. Hoesch, Liam Gannon, Kenya Shimada, Benjamin J. Parrett, Matthew D. Watson, Timur K. Kim, Xiangde Zhu and Cedomir Petrovic, *Phys. Rev. Lett.* 122, 017601 (2019).
[25] A. Baum, A. Milosavljevic, N. Lazarevic, M. M. Radonjie, B. Nikolic, M. Mitschek, Z. Inanloo Maranloo, M. Scepanovic, M. Grujic-Brojcin, N. Stojilovic, M. Opel, Aifeng Wang, C. Petrovic, Z. V. Popovic and R. Hackl, Phys. Rev. B 97, 054306 (2018).

[26] A. Glamazda, P. Lemmens, J. M. Ok, Jun Sung Kim, and K.-Y. Choi, Phys. Rev. B 99, 075142 (2019).

[27] A. Baum, H. N. Ruiz, N. Lazarevic, YaoWang, T. Böhm, R. Hosseinian Ahangharenjejad, P. Adelmann, T. Wolf, Z. V. Popovic, B. Moritz, T. P. Deveraux and R. Hackl, Communications Physics 2, 14 (2019).

[28] P. Massat, Donato Farina, Indranil Paul, Sandra Karlsson, Pierre Strobel, Pierre Toulemonde, Marie-Aude Méasson, Maximilien Cazayous, Alain Sacuto, Shigeru Kasahara, Takasada Shibauchi, Yuji Matsuda and Yann Gallais, Proc. Natl. Acad. Sci. USA 113, 9177 (2016).

[29] H. Ruiz, Yao Wang, Brian Moritz, Andreas Baum, Rudi Hackl, and Thomas P. Devereaux, Frustrated magnetism from local moments in FeSe. Phys. Rev. B 99, 125130 (2019).

[30] Defa Liu, Cong Li, Jianwei Huang, Bin Lei, Le Wang, Xianxin Wu, Bing Shen, Qiang Gao, Yuxiao Zhang, Xu, Liu, Yong Hu, Yu Xu, Aiji Liang, Jing Liu, Ping Ai, Lin Zhao, Shaolong He, Li Yu, Guodong Liu, Yiyuan Mao, Xiaoli Dong, Xiaowen Jia, Fengfeng Zhang, Shenjin Zhang, Feng Yang, Zhimin Wang, Qiujuan Peng, Youguo Shi, Jiangping Hu, Tao Xiang, Xianhui Chen, Zuyan Xu, Chuangtian Chen and X. J. Zhou, Phys. Rev. X 8, 031033 (2018).

[31] A. Kreisel, Brian M. Andersen, P. O. Sprau, A. Kostin, J. C. Séamus Davis, and P. J. Hirschfeld, Phys. Rev. B 95, 174504 (2017).

[32] L. C. Rhodes, Matthew D.Watson, Amir A. Haghighirad, Daniil V. Evtushinsky, Matthias Eschrig, and Timur K. Kim, Phys. Rev. B 98, 180503 (2018).

[33] A. Kostin, P. O. Sprau, A. Kreisel, Yi Xue Chong, A. E. Böhmer, P. C. Canfield, P. J. Hirschfeld, B. M. Andersen and J. C. Séamus Davis, Nature Mater. 17, 869 (2018).
Figures:

Fig. 1. (Color online) Electrical resistivity and Mössbauer spectrum. Normalized in-plane resistivity for FeSe$_{1-x}$S$_x$. (a, b). The left inset in (a) shows the $d(\rho_T/\rho_{300K})/dT$ around the structural transition, $T_s$ is inferred by the dip of $d(\rho_T/\rho_{300K})/dT$ and indicated by the arrow. (c) Ratio of resistivity at 300 K to resistivity at 14 K and resistivity values at 14 K (d) Exponent $\alpha$ in resistivity (see text). Mössbauer spectrum recorded in low velocity range at 295 K of the tetragonal FeSe$_{0.31}$S$_{0.69}$ (e) and of the tetragonal FeSe$_{0.82}$S$_{0.18}$ (f).

Fig. 2. (Color online) Average and local structural parameters. (a, b) Lattice parameters $a$, $c$ and $c/a$ ratio. Open (full) symbols represent refinement results from laboratory (synchrotron) data. (c, d) Normalized XANES spectra of FeSe$_{1-x}$S$_x$ measured at Fe K-edge and Se K-edge. The features in the Fe K-edge XANES are denoted by A, B, C; Se K-edge are denoted by D, E. (e, f) Fourier transform (FT) magnitudes of the $k^2$-weighted EXAFS oscillations at Fe K-edge and Se K-edge. (g) Crystal structure of FeSe. (h) Fe-Fe, FeSe, and FeS distances determined by EXAFS as a function of $x$. The
Fe-Se and Fe-S bond distances show weak changes for all $x$ and remain close to values observed in the end member compounds FeSe and FeS.

Fig. 3. (Color online) FeSe$_{1-x}$S$_x$ ($0 \leq x \leq 1$) phase diagram. The composition-temperature ($x$ - T) phase diagram for FeSe$_{1-x}$S$_x$ single crystals (a) with its three major parts: nematic for $x \leq 0.17$, Fermi liquid for $x \geq 0.9$ and the largest, middle part. Crystallographic disorder is evaluated via full width at half maximum (FWHM)$^{-1}$ of single crystal diffraction (XRD) [001] and Raman ($\text{A}_{1g}$, $\text{B}_{1g}$) peaks, all normalized to FeSe. For clarity and since for FeSe $T_c = 10$ K, we show $T_c(x)$ and not $T_c(x)/T_c(\text{FeSe})$. Smaller (FWHM)$^{-1}$ i.e. larger FWHM indicates higher disorder. The [FWHM XRD]$^{-1}$ relates to crystallographic c-axis Bragg plane disorder. The disorder is also estimated via the dc-transport-related residual resistivity ratio $\text{RRR}(x)/\text{RRR}(\text{FeSe})$; smaller values indicate higher disorder. ARPES band structure near the $\Gamma$ point for FeSe$_{0.97}$S$_{0.03}$ (b) showing the $\alpha$, $\beta$ and $\gamma$ bands near the Fermi level and the $\varepsilon$ band at about 0.24 eV below. Evolution (c) of the binding energy of the clearly resolvable $\varepsilon$ band with $x$; note that the rapid change of the binding energy coincides with the increase in RRR in (a). Fermi surface near the $\Gamma$ point in the Brillouin zone for FeSe$_{0.9}$S$_{0.1}$ (d), FeSe$_{0.52}$S$_{0.48}$ (e) and FeSe$_{0.31}$S$_{0.69}$ (f). In panel (a) we plot the inverse electronic scattering rate $1/\tau$ normalized to FeSe$_{0.97}$S$_{0.03}$. The smearing of the Fermi surfaces gives an impression of the scattering rates. Numbers are derived from the energy dispersion curves in Ref. 15. High $1/\tau$ is a hallmark of disorder-related electron scattering. The fact that $T_c(x)$ is closely connected with the scattering strength for vast region in the phase diagram points to an order parameter with nodes that gets averaged over the Fermi surface and thus reduced by scattering along with $T_c$. 

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Supplement for: Superconducting Order from Local Disorder

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11. Supplementary references

1. Crystal growth

Single crystals of FeSe$_{1-x}$S$_x$ with 0 ≤ $x$ ≤ 0.24 were grown using an eutectic mixture of the KCl and AlCl$_3$ as the transport agent [1,2]. Single crystals of FeSe$_{1-x}$S$_x$ with 0.4 ≤ $x$ ≤ 1 were synthesized by deintercalation of potassium from the corresponding K$_{0.8}$Fe$_{2-y}$(Se$_{1-x}$S$_x$)$_2$ single crystals using the hydrothermal reaction method [3].

2. Resistivity

The dependence on substitution $x$ of room temperature resistivity of FeSe$_{1-x}$S$_x$ is shown in Table S1. The values decrease from 0.54 m$\Omega$ cm to 0.3 m$\Omega$ cm at $x = 0.03$ and are nearly constant with further doping. For $x = 0.4$ higher room temperature resistivity values are observed up to $x = 1$ where $\rho$(300K) = 0.13 m$\Omega$ cm.
TABLE S1. Room temperature resistivities of FeSe<sub>1−x</sub>S<sub>x</sub> single crystals (0 ≤ x ≤ 1). Values for x ≤ 0.34 are shown in 10<sup>−1</sup> mΩcm whereas values for x ≥ 0.4 are shown in mΩcm.

| x  | 0   | 0.03 | 0.05 | 0.07 | 0.10 | 0.11 | 0.14 | 0.16 | 0.18 | 0.23 | 0.39 | 0.48 | 0.59 | 0.69 | 0.84 | 0.90 | 0.93 | 1   |
|----|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-----|
| ρ  | 5.0 | 3.2  | 3.0  | 3.6  | 2.5  | 3.2  | 3.2  | 4.0  | 2.8  | 4.2  | 2.6  | 2.3  | 1.7  | 2.9  | 2.6  | 2.1  | 1.5  | 0.25 | 0.13 |

Optimally doped Ba(Fe<sub>1−x</sub>Cox)₂As₂, NaFe<sub>1−x</sub>CoxAs, BaFe₂(As₁−xPx)₂ and FeSe at an applied pressure inducing maximal T<sub>c</sub> all feature linear normal-state resistivities just above T<sub>c</sub> [4-7]. A near linear temperature dependence of the resistivity in FeSe₁−xS<sub>x</sub> is also present for small x where there is a rise of T<sub>c</sub> in comparison to unsubstituted FeSe [Fig. 1(d) in the main text] [8]. Another common feature of the phase diagrams of unconventional superconductors is a transition to a Fermi-liquid state when doping is increased from optimal to overdoping, frequently associated with the antiferromagnetic spin fluctuation mechanism [9]. Although long-range magnetic order is absent in both FeS and FeSe [Fig. 1(e) and 1(f) in the main text, see also section 3 below], there are strong magnetic fluctuations and magnetic order is induced by pressure [10].

Changes in RRR and ρ₁₄K with x cannot be explained by the influence of the synthesis method on the crystal quality. FeS is synthesized by hydrothermal method, yet it features low defect scattering, low residual resistivity and relatively high RRR that allows for the observation of quantum oscillations just like FeSe synthesized by chemical vapor transport [11,12]. It is of interest to note that BaFe₂(As₁−xPx)₂ crystal alloys do not show any significant reduction of the mean free path when compared to BaFe₂As₂ [13]. This indicates a subtler influence of Se/S substitution.

3. Mössbauer experiment

The spectrometer was calibrated by the spectrum of a natural iron foil. The spectra were collected from samples in low and high velocity range. All Mössbauer spectra have been examined by the WinNormos-Site software package based on the least square method [14]. The measured isomer shift values (δ) are given relative to metallic alpha iron (δ = 0).

In order to study the local structure of Fe ions at a 2a Wyckoff site of the P4/nmm space group it is instructive to consider the coordination spheres of the iron probe. The four nearest neighbors (NN) chalcogen atoms make the surrounding FeCh<sub>4</sub> (Ch=Se,S) tetrahedron. The next-nearest-neighbors (NNN) are two metal shells with four iron atoms in each shell. Farther behind are two chalcogen shells which consist of four and eight chalcogen atoms, respectively. The nearer four are situated in the same atomic plane with the iron probe. The first half of farther eight atoms are above and the second half are below this plane stacked along the c-axis. The symmetry point group of the Fe atomic site in β-FeS and α-FeSe is 4m2. The non-ideal tetrahedral surrounding of Fe results in a non-spherical charge distribution around the probe and the emergence of an electric field gradient (EFG) [15,16]. Substitution of different chalcogen atoms in an iron-chalcogenide material additionally breaks the Fe local symmetry, causing more pronounced EFG. Replacement of sulfur by selenium atoms defines a new Se-containing atomic plane which is different from iron and sulfur planes in FeS [15]. In pure materials, the bond distance d<sub>Fe−Se</sub> in α-FeSe is ~ 10% longer than d<sub>Fe−S</sub> in β-FeS [16]. The Se-plane in FeSe is farther away from the Fe-plane than the S-plane in FeS.
expanding the crystal along the c-axis. In FeSe$_{1-x}$S$_x$ single crystal alloys the number of occupied chalcogen sites in the Se or S planes depends on the Se/S atomic ratio. This leads to many nonequivalent Fe sites in contrast to the uniform chalcogen surrounding in pure FeS or FeSe. It is expected that Mössbauer spectroscopy will detect a distribution of quadrupole splittings (Δ) because of different EFGs.

The binomial distribution describes the probability for the appearance of coordination spheres of the Fe atom with different content of the S and Se ions [17]:

$$p(z_1, \ldots z_k, n_1, \ldots n_k, c) = \prod_{i=1}^{k} p_{z_i}^{n_i}(c) = \prod_{i=1}^{k} \left(\frac{Z_i}{n_i}\right)^{n_i}(1-c)^{z_i-n_i}$$  

Where $0 \leq n_i \leq z_i$ and $p$ is probability mass function (PMF). PMF describes probability of having $n_i$ impurities on $z_i$ host sites of the i-th shell for impurity concentration c. Considering only the tetrahedron with four NN for $c = 0.3$, the equation 1 gives approximately the ratio $p(n_1 = 0):p(n_1 = 1):p(n_1 = 2):p(n_1 = 3):p(n_1 = 4) = 24:41:26:8:1$. Hence, the Δ-distribution by means of the doublets with Lorentz lines with area ratio follows the PMF ratio. The experimental spectra (Fig. S1) can only be fit with the three doublet fitting model where one of the doublet collapsed into a single line in the spectrum of the tetragonal FeSe$_{0.31}$S$_{0.69}$ (Table S2). This is to be expected since it originates from the tetrahedron without Se atoms where a very low Δ value was measured [15,18]. When S substitutes Se in FeSe$_4$ the subspectrum with the largest area is assigned to the FeSe$_4$ tetrahedron [19,20]. The other two doublets in both spectra arise from Se atom in FeS$_4$ tetrahedra, or vice versa, the existence of at least one S on the FeSe$_4$ tetrahedron corners.

Wider lines and the large hyperfine parameter uncertainties are consequences of a great number of spatial combinations of substituted atoms. Bader analyses of the pure iron chalcogenides shows that there is a larger charge transfer from the Fe atom to the S atom than to the Se atom [16]. The charge transfer changes the chemical shift, i.e. δ. Therefore, the value of δ is the result of a competition between electron occupation on 4s- and 3d-orbitals of the Fe [21]. According to the Bader analysis there is a bond critical point between the NN chalcogen ion and the NNN chalcogen from the adjacent layer in the fifth shell [16]. There are significant probabilities for the next PMF: $p(n_1 = 0, n_5 = 2, 3)$, $p(n_1 = 1, n_5 = 1, 2, 3, 4)$, and $p(n_1 = 2, n_5 = 1, 2, 3)$. All contribute to changes in the probe electron density, additionally smearing the quadrupole distribution with consequences on the subspectrum area ratio. Therefore, our data confirm the randomness of the spatial distribution of the Se and S atoms in FeSe$_{1-x}$S$_x$.

| Sample       | $A$ (%) | Γ (mms$^{-1}$) | δ (mms$^{-1}$) | Δ (mms$^{-1}$) |
|--------------|---------|----------------|----------------|----------------|
| FeSe$_{0.31}$S$_{0.69}$ | 16(5)   | 0.221$^{\dagger}$ | 0.351(5)       |                |
|              | 47(10)  | 0.57(7)        | 0.355(9)       | 0.14(14)       |
|              | 37(9)   | 0.22(2)        | 0.401(5)       | 0.214(6)       |
| FeSe$_{0.82}$S$_{0.18}$ | 45(3)   | 0.244(8)       | 0.431(2)       | 0.282(4)       |
|              | 43(4)   | 0.51(1)        | 0.350(4)       | 0.55(3)        |
|              | 12(1)   | 0.221$^{\dagger}$ | 0.248(7)       | 0.19(2)        |

4. **Diamagnetic signal and X-ray diffraction**

The superconducting $T_c$ values inferred from the diamagnetic signal [Figs. S2(a-c)] are consistent with those determined by resistivity. Both underdoped and overdoped samples show relatively sharp transitions in
contrast to relatively broad ones observed in the range \((0.21 \leq x \leq 0.70)\). The onset of the diamagnetic signal is observed when the resistivity [Fig. 1(a,b) main text] drops to zero. Close inspection shows that the transition starts to broaden when \(T_s\) is completely suppressed. With further S substitution the samples \(x = 0.21\) and \(x = 0.24\) exhibit wide transitions, and full shielding fractions are established at only 3.9 and 3.2 K, respectively, whereas the crystal for \(x = 0.48\) probably shows percolative superconductivity.

All the single crystal X-ray diffraction (XRD) patterns [Fig. S2(d)] show (00l) reflections. The reflections shift to higher scattering angles with increasing \(x\), indicating the decrease of the unit cell volume. Typical Rietveld refinement of the average unit cell from the synchrotron powder X-ray diffraction data is shown in Fig. S2(e). Synchrotron X-ray powder diffraction patterns (Fig. S3) confirm the phase purity of FeSe\(_{1-x}\)S\(_x\) for all investigated crystals in the range \(0 \leq x \leq 1\); the small Fe\(_3\)O\(_4\) peaks visible for some \(x\) are due to oxidation during pulverization of air-sensitive crystals for 1 mm polyamide capillary loading. Note the excellent agreement in lattice parameters obtained by two different instruments [Fig. 2(a,b) in the main text] and by two refinement methods: Le Bail (laboratory) and Rietveld (synchrotron data). The evolution of the lattice parameters [Fig. 2(a), main text] is different from the FeSe pressure effect where \(2c/(a+b)\) decreases smoothly up to 4 GPa and then increases up to 9 GPa where the tetragonal crystal structure transforms to hexagonal FeSe[22].

5. XANES and EXAFS

The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) spectra were processed and analyzed using the ATHENA and ARTEMIS software programs [23]. The AUTOBK code was used to normalize the absorption coefficient, and to separate the EXAFS signal, \(\chi(k)\), from the atom-absorption background. The extracted EXAFS signal, \(\chi(k)\), was weighed by \(k^2\) to emphasize the high-energy oscillation and then Fourier-transformed in a \(k\) range from 2 to 5 Å\(^{-1}\) to analyze the data in \(R\) space.

EXAFS could be described in the single-scattering approximation [24]:

\[
\chi(k) = \sum_i N_i S_i^2 f_i(kR_i) e^{-2kR_i/\lambda} e^{-2k^2\sigma_i^2} \sin[2kR_i + \delta_i(k)]
\]

where \(N_i\) is the number of neighbouring atoms at a \(R_i\) distance from the photoabsorbing atom, \(S_i^2\) is the passive electrons reduction factor, \(f_i(kR_i)\) is the backscattering amplitude, \(\lambda\) is the photoelectron mean free path, \(\delta_i\) is the phase shift of the photoelectrons, \(k\) is photon wavenumber and \(\sigma_i^2\) is the correlated Debye-Waller
factor measuring the mean square relative displacement of the photoabsorber-backscatter pairs. The first nearest neighbors of Fe atoms are four Se atoms located at 2.395 Å, and the next nearest neighbors are four Fe atoms at 2.668 Å [22]. The first nearest neighbors of Se atoms are four Fe atoms at 2.395 Å tetrahedral distances. Local structural information, such as the bond distance and Debye-Waller factor, were obtained by the best-fit model. The features above 3 Å are due to longer distances and multiple scattering effects.

X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine-structure (EXAFS) provide important information on the hybridization between the Fe 3d and Ch 4p orbitals as well as accurate Fe-Ch bond distances [25]. Typical features of the Fe K-edge XANES are denoted as A, B, C, whereas those of the Se K-edge are denoted as D, E [Fig. 2(c,d) in the main text]. The pre-peak A is due to the direct 1s → 3d quadrupole transition to unoccupied states, with a contribution of dipole transition from the Fe 1s to unoccupied Fe 3d - Se 4p hybrid bands [26]. The edge feature B is determined by the 1s → 4p transitions whereas feature C results from the 1s → 4p state with a significant admixture to the Ch d states. The intensity of A increases with S concentration, indicating an increase of the Fe 3d - Se 4p hybridization. This is consistent with the very weak reduction of the Fe-Se bond length with doping. The decrease of the intensity of structure C indicates the reduction of the hybridization of Fe 4p and Se d states due to low Se concentration. The results for the Se K-edge are consistent with those for the Fe K-edge, in which peak D is due to 1s → 4p dipole transition and feature E is the result of multiple scattering of the photoelectrons with the nearest neighbors.

The increase of D with x is consistent with the increase of A and the stronger hybridization of Fe 3d-Se/S 4p bands. The doping dependence of the Fe and Se K-edge XANES features resembles those observed in high pressure measurement and is opposite to effects induced by Te substitution [25,27]. Increased d-p hybridization is expected to promote delocalization [28]. Since the first shell of the Se K-edge is well separated from the distant shells, we fit the Se K-edge EXAFS using a model with a single distance and take only the main peaks of the Fe-edge into consideration. Interestingly, the fitting can only be improved by using different values of Fe-Se and Fe-S bond lengths [Fig. 3(g) in the main text], similar to FeTe_{1-x}Se_x [29]. The derived bond lengths are presented in Fig. 2(h) in the main text.

### 6. Weak vs. strong disorder

Here we comment on the validity of the Anderson theorem for all x in FeSe_{1-x}S_x. As long as k_Fl≫1, where k_F is a Fermi wave vector and l is a mean free path, the superconducting T_c in isotropic s-wave superconductor is unaffected by nonmagnetic impurities [30,31]. We estimate k_Fl in our samples as follows. In Boltzmann theory the 2D resistivity is: $\rho = (\hbar/e^2)(d/k_Fl)$ where $\hbar$ is the Planck constant, e is the elementary charge, k_F is the Fermi wave number, and d is interplane distance and l is mean free path. Approximating d by the value of lattice parameter c [Fig. 2(a) in the main text] and using the experimental $\rho$ values [Fig. 1(c) main text], we plot k_Fl vs. x in Fig. S4.

### 7. ARPES scattering rates

To measure the electronic structure, we took several momentum cuts along Γ-M direction using incoming photon energy $h\nu = 120$ eV and circular polarization. From the different cuts, we reconstruct the Fermi surface as shown in Figure S5. To examine the scattering rate, we measure the band dispersion along the high symmetry line Γ-M direction using a low incoming photon energy of $h\nu = 25$ eV to obtain high-resolution measurements both in energy and momentum. For each cut acquired from a sample with different x, we extract the energy distribution curve (EDC) at momentum $k_F$ of the outer band defined as the peak at minimal binding
energy with respect to the Fermi energy and have the larger $k_F$ value. The EDCs were normalized to their high binding energy values and the background was removed by subtracting an EDC measured deep in the unoccupied region. To estimate the influence of sulfur on the scattering rate, we have fitted the EDC to the two Lorentzians corresponding to the two bands. The width of the Lorentzian peak near the Fermi energy can be considered as a measure that tracks the evolution of the scattering rate with doping.

![FIG S5. Scattering rates from ARPES. Energy distribution curves and fitted Lorentzians for FeSe$_{0.9}$S$_{0.1}$ (a), FeSe$_{0.52}$S$_{0.48}$ (b) and FeSe$_{0.31}$S$_{0.69}$ (c).](image)

8. Theory: DFT+DMFT Scattering rates

Our density functional theory plus dynamical mean field theory (DFT+DMFT) calculations were performed at the fully charge self-consistent level [32] at 116 K. The DFT calculations were performed within Perdew-Burke-Ernzehof generalized gradient approximation (PBE-GGA) [33] as implemented in WIEN2K [34]. The DMFT effective impurity problem was solved using continuous time quantum Monte Carlo [35], within a Hubbard $U = 5.0$ eV and Hund’s coupling $J = 0.8$ eV.

In both FeSe and FeS near the Fermi energy around the Γ point the electronic states are composed by distinct mixtures of Fe $3d$ orbitals [36-38]. In addition, the average anion height above Fe plane relates to the hole pocket of $d_{xy}$ orbital character [39]. To investigate the degree of electronic correlations in the FeSe$_{0.5}$S$_{0.5}$ we construct a model using a (2x2) supercell where we have an equal amount of Se and S atoms. From our DFT+DMFT calculations we evaluate the quasiparticle scattering rate at $T = 116$ K from the extrapolation of the imaginary-frequency self-energy to zero: $\Gamma = -Z_\alpha \frac{\partial}{\partial \omega} \left( \sum_{\sigma} \langle i0^+ \rangle \right)$ where $\alpha$ is orbital index and $Z_\alpha$ is the quasiparticle weight [40,41]. The quasiparticle weight, in turn, is evaluated as $Z_\alpha^{-1} = \frac{\partial}{\partial \omega} \left( \sum_{\sigma} \langle i0^+ \rangle \right)_{\omega \rightarrow 0^+}$. To investigate the effect of the alloying we considered the experimental lattice parameters measured to FeSe$_{0.5}$S$_{0.5}$ in our calculations for FeSe, FeSe$_{0.5}$S$_{0.5}$, and FeS. In unrelaxed structures (U) Fe-Ch (Ch = Se,S) the bond distances were constrained to the EXAFS experimental bond distances (Fig. 2 main text; Fe-Se = 2.395 Å and Fe-S = 2.265 Å) whereas after the structural relaxation (R) the distances between atoms are slightly increased (Fe-Se = 2.427 Å and Fe-S = 2.301 Å). For our FeSe$_{0.5}$S$_{0.5}$ model we found largest scattering rates for the electronic states associated with Fe-$d_{xy}$ orbitals. In Table S3 we display the obtained $d_{xy}$ scattering rates for the pristine systems as well as for the alloy. The orbital and site averaged scattering rates for the latter are shown in Table S4.

From Tables S3 and S4 it is evident that $d_{xy}$ scattering rates are very sensitive to Fe-Se and Fe-S bond lengths. The total scattering for FeSe$_{0.5}$S$_{0.5}$, obtained as the site and orbital average scattering rates, is around 3.3 meV (Table S4). On the other hand, the orbital averaged scattering rates for FeSe and FeS (relaxed structures) are 11.3 and 2.1 meV, respectively. Within DFT+DMFT framework larger scattering
rates correspond to increase in electronic incoherence of states near the Fermi energy. This indicates that scattering rate due to solely local electronic correlations are reduced along the increasing of $x$ in FeSe$_{1-x}$S$_x$ systems. However, the calculated scattering rates are very small when compared to ARPES scattering rates at $\Gamma$ point obtained for our samples. Whereas the degree of correlations within the model is governed by Fe-Se and Fe-S bond distances, experimental scattering rate changes in FeSe$_{1-x}$S$_x$ ($0 \leq x \leq 1$) cannot be explained by the decrease of electronic correlations as S substitutes Se in the lattice.

Table S3. DFT+DMFT $d_{xy}$ scattering rates. Calculated scattering rates (in meV) are shown for unrelaxed (U) and relaxed (R) crystal structures of FeSe, FeSe$_{0.5}$S$_{0.5}$, and pure FeS.

| Structure   | FeSe | FeSe$_{0.5}$S$_{0.5}$ | FeS |
|-------------|------|-----------------------|-----|
| $1/\tau d_{xy}$ (meV) - U | 5.6  | 1.9                   | 1.2 |
| $1/\tau d_{xy}$ (meV) - R  | 14.4 | 5.9                   | 4.4 |

Table S4. DFT+DMFT orbital and site averaged scattering rates (meV) for FeSe$_{0.5}$S$_{0.5}$. Calculated scattering rates are shown in meV.

| Fe site | $d_{xy}$ | $d_{xz}$ | $d_{yz}$ | $d_{z^2}$ | $d_{x^2-y^2}$ |
|---------|----------|----------|----------|-----------|--------------|
| Fe1     | 7.8      | 3.9      | 5.8      | 0.7       | 0.6          |
| Fe2     | 3.6      | 3.7      | 4.1      | 0.4       | 0.4          |
| Fe3     | 6.6      | 4.6      | 4.5      | 1.3       | 2.6          |
| Fe4     | 5.6      | 2.8      | 4.5      | 0.3       | 1.5          |
| Average | 5.9      | 3.8      | 4.7      | 0.7       | 1.3          |

9. Raman spectroscopy

As an excitation source solid state laser emitting at 532 nm was used. In our scattering configuration, the plane of incidence is the $ab$ plane, with incident (scattered) light propagation along the $c$-axes. Right before being placed in vacuum samples were cleaved in the air. All measurements were performed in high vacuum ($10^{-6}$ mbar) using a KONTI CryoVac continuous Helium flow cryostat with 0.5 mm thick window. The laser beam was focused using microscope objective with x50 magnification. All spectra were corrected for Bose factor.

Fig. S6 shows Raman shift and Lorentzian line widths of the $A_{1g}$ and $B_{1g}$ Raman modes at 100 K. In the absence of Fano-shape peak distortions, peak width gives a caliper of phonon vibrations-related crystallographic disorder. Larger FWHM is consistent with higher disorder. For better comparison with changes in superconducting $T_c$, in main text Fig. 3(a) we plot $[\text{FWHM}(x)]^{-1}$, normalized to $[\text{FWHM}(0)]^{-1}$.

10. Comparison of pressure and S doping

![FIG S6. Raman spectroscopy of FeSe$_{1-x}$S$_x$ ($0 \leq x \leq 1$). Raman shift and Lorentzian line widths of the $A_{1g}$ and $B_{1g}$ modes.](image)
When the applied and chemical pressure in the FeSe phase diagram are scaled by the structural transition temperature (6 GPa for full S occupancy), $T_c (x)$ and $T_c (P)$ agree reasonably well with each other [Fig. S7(a)] up to about the NCP [4]. Beyond the NCP there is a local minimum of $T_c (P)$ at around 1.5 GPa and magnetic order appears with the increase in $T_c$ up to 30 K whereas $T_c$ in FeSe$_{1-x}$ decreases to a minimum at $x = 0.4$ and increases with further doping. Thus, S substitution provides mainly chemical pressure effects for $x$ values below the NCP. This is also evident from the $a$ lattice parameter [Fig. 2(a) main text] that decreases by $x = 0.16$ to about 3.75 Å, consistent with pressurized FeSe [42]. It is instructive to stay focused on the nematic region and to compare $T_c (Ts)$ induced by S substitution with pressure and disorder [Fig. S6(b)] [4,43,44]. The $T_c (Ts)$ values in FeSe$_{1-x}$ and pressurized FeSe have similar dome-like behavior with the highest $T_c$ at $Ts \sim 60$ K; in contrast $T_c$ decreases quickly with the suppression of $Ts$ in FeSe disordered by small variations in the synthesis conditions. In our crystals sulfur substitutes selenium in a random-alloy manner [Fig. 1(e,f) main text] hence it entails both pressure and disorder. Since there is no comparably dramatic increase in $T_c$ as in FeSe under pressure [42], it is plausible to conclude that disorder counterbalances pressure for $x$ up to the NCP where the abrupt change of superconducting gap takes place [45,46].

11. Supplementary references:

1. Rongwei Hu, Hechang Lei, Milinda Abeykoon, Emil S. Bozin, Simon L. Billinge, J. B. Warren, Theo Siegrist and C. Petrovic, Phys. Rev. B 83, 224502 (2011).
2. D. Chareev, Evgeniy Osadchii, Tatiana Kuzmicheva, Jiunn-Yuann Lin, Svetoslaw Kuzmichev, Olga Volkova and Alexander Vasiliev, Crystengcomm 15, 1989 (2013).
3. Christopher K. H. Borg, Xiuquan Zhou, Christopher Eckberg, Daniel J. Campbell, Shanta R. Saha, Johnpierre Paglione, and Efrain E. Rodriguez, Phys. Rev. B 93, 094522 (2016).
4. J. P. Sun, K. Matsuura, G. Z. Ye, Y. Mizukami, M. Shimozawa, K. Matsubayashi, M. Yamashita, T. Watashige, S. Kasahara, Y. Matsuda, J. -Q. Yan, B. C. Sales, Y. Uwatoko, J. -G. Cheng and T. Shibauchi, Nat. Commun. 7, 12146 (2016).
5. A. F. Wang, X. G. Luo, Y. J. Yan, J. J. Ying, Z. J. Xiang, G. J. Ye, P. Cheng, Z. Y. Li, W. J. Hu, and H. H. Chen, Phys. Rev. B 85, 224521 (2012).
6. Jiun-Haw Chu, James G. Analytis, Chris Kucharczyk, and Ian R. Fisher, Phys. Rev. B 79, 014506 (2009).
7. S. Kasahara, T. Shibauchi, K. Hashimoto, K. Ikada, S. Tonegawa, R. Okazaki, H. Shishido, H. Ikeda, H. Takeya, K. Hirata, T. Terashima, and Y. Matsuda, Phys. Rev. B 81, 184519 (2010).
8. Yoshikazu Miziguchi, Fumiaki Tomioka, Shunsuke Tsuda, Takahide Yamaguchi and Yoshihiko Takano, J. Phys. Soc. Jpn. 78, 074712 (2009).
9. R. A. Cooper, Y. Wang, B. Vignolle, O. J. Lipscombe, S. M. Hayden, Y. Tanabe, T. Adachi, Y. Koike, M. Nohara, H. Takeshi, Cyril Proust and N. E. Hussey, Science 323, 603 (2009).
10. M. Bendele, A. Amato, K. Conder, M. Elender, H. Keller, H.-H. Klauss, H. Luetkens, E. Pomjakushina, A. Raselli, and R. Khasanov, Phys. Rev. Lett. 104, 087003 (2010).
11. Taichi Terashima, Naoki Kikugawa, Hai Lin, Xiyu Zhu, Hai-Hu Wen, Takuya Nomoto,
Katsuhiro Suzuki, Hiroaki Ikeda, and Shinya Uji, Phys. Rev. B 94, 100503(R) (2016).
12. Taichi Terashima, Naoki Kikugawa, Andhika Kiswadhi, Eun-Sang Choi, James S. Brooks, Shigeru Kasahara, Tatsuya Watashige, Hiroaki Ikeda, Takasada Shibachi, Yuji Matsuda, Thomas Wolf, Anna E. Böhmer, Frédéric Hardy, Christoph Meingast, Hilbert v. Löhneysen, Michi-To Suzuki, Ryotaro Arita, and Shinya Uji, Phys. Rev. B 90, 144517 (2014).
13. J. G. Analytis, J.-H. Chu, R. D. McDonald, S. C. Riggs, and I. R. Fisher, Phys. Rev. Lett. 105, 207004 (2010).
14. Brand, R. A. WinNormos Möossbauer fitting program, Universität Duisburg 2008.
15. Aifeng Wang, Lijun Wu, V. N. Ivanovski, J. B. Warren, Jianjun Tian, Yimei Zhu, and C. Petrovic, Phys. Rev. B 94, 094506 (2016).
16. V. Koteski, V.N.Ivanovski, A.Umićević, J.Belošević-Cavor, D.Toprek and H.-E.Mahnke, J. Magn. Magn. Mater. 441, 769 (2017).
17. I. Vincze and A. I. Campbell, J. Phys. F: Met. Phys. 3, 647 (1973).
18. S. Holenstein, U. Pachmayr, Z. Guguchia, S. Kamusella, R. Khasanov, A. Amato, C. Baines, H.-H. Klauss, E. Morenzoni, D. Johrendt, and H. Luetkens, Phys. Rev. B 93, 140506 (2016).
19. A.Blachowski, K. Ruebenbauer, J. Zukrowski, J. Przewoźnik, K. Wojciechowski and Z. M. Stadnik, J. Alloys Compd. 494, 1 (2010).
20. A. Skylarova, J. Linden, G. C. Tewari, E.-L. Rautama and M. Karppinen, Hyperfine Interactions 226, 341 (2014).
21. F. Menil, J. Phys. Chem. Solids 46, 763 (1985).
22. S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takano, T. Kagayama, T. Nakagawa, M. Takata, and K. Prassides, Phys. Rev. B 80, 064506 (2009).
23. B. Ravel, B. and M. J. Newville, Synchrotron Radiat. 12, 537 (2005).
24. R. Prins and D. S. Koningsberger (eds.), X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, XANES (Wiley, New York, 1988).
25. M. Bendele, C. Marini, B. Joseph, L. Simonelli, P. Dore, S. Pascarelli, M. Chikovani, E. Ponomjakushina, K. Conder, N. L. Saini and P. Postorino, J. Phys.: Condens. Matter 25, 425704 (2013).
26. Frank de Groot, Gyorgy Vanko and Pieter Glatzel, J. Phys.: Condens. Matter 21, 104207 (2009).
27. B. Joseph, A. Iadecola, L. Simonelli, Y. Mizuguchi, Y. Takano, T. Mizokawa and N. L. Saini, J. Phys.: Condens. Matter 22, 485702 (2010).
28. Jun Ishizuka, Takemi Yamada, Yuki Yanagi and Yoshiaki Ono, Fermi Surface, J. Phys. Soc. Jpn. 87, 014705 (2018).
29. M. Y. Hacisalihoglu, E. Paris, B. Joseph, E. Yanmaz and N. L. Saini, Phys. Chem. Chem. Phys. 17, 18131 (2015).
30. P. Anderson, Phys. Rev. 109, 1492 (1958).
31. P. Anderson, J. Phys. Chem. Solids 11, 26 (1959).
32. K. Haule, C.-H. Yee and K. Kim, Phys. Rev. B 81, 195107 (2010).
33. John P. Perdew, Kieron Burke, and Matthias Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
34. P. Blaha, P. Karlheinz Schwarz and Georg K. H. Madsen, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001).
35. K. Haule, Phys. Rev. B 75, 155113 (2007).
36. A. Kostin, P. O. Sprau, A. Kreisel, Yi Xue Chong, A. E. Böhmer, P. C. Canfield, P. J. Hirschfeld, B. M. Andersen & J. C. Seamus Davis, Nat. Mater. 17 869 (2018).
37. M. Yi, H. Pfau, Y. Zhang, Y. He, H. Wu, T. Chen, Z. R. Ye, M. Hashimoto, R. Yu, Q. Si, D.-H. Lee, Pengcheng Dai, Z.-X. Shen, D. H. Lu, and R. J. Birgeneau. Phys. Rev. X 9, 041049 (2019).
38. J. Miao, X. H. Niu, D. F. Xu, Q. Yao, Q. Y. Chen, T. P. Ying, S. Y. Li, Y. F. Fang, J. C. Zhang, S. Ideta, K. Tanaka, B. P. Xie, D. L. Feng, and Fei Chen, Phys. Rev. B 95, 205127 (2017).
39. Kazuhiko Kuroki, Hidetomo Usui, Seiichiro Onari, Ryotaro Arita, and Hideo Aoki, Phys. Rev. B 79, 224511 (2011).
40. P. Zhang, R. E. Cohen and K. Haule, Nature 517, 605 (2015).
41. L. V. Pourovskii, T. Miyake, S. I. Simak, A. V. Ruban, L. Dubrovinsky, and I. A. Abrikosov, Phys. Rev. B 87, 115130 (2013).
42. S. Medvedev, T. M. McQueen, I. A. Troyan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann and C. Felser, Nature Mater. 8, 630 (209).
43. A. E. Böhmer, V. Taufour, W. E. Straszheim, T. Wolf, and P. C. Canfield, Phys. Rev. B 94, 024526 (2016).
44. Sahana Rößler, Chien-Lung Huang, Lin Jiao, Cevriye Koz, Ulrich Schwarz, and Steffen Wirth, Phys. Rev. B 97, 094503 (2018).
45. Yuki Sato, Shigeru Kasahara, Tomoya Taniguchi, Xiangzhuo Xing, Yuichi Kasahara, Yoshifumi Tokiwa, Youichi Yamakawa, Hiroshi Kontani, Takasada Shibauchi and Yuji Matsuda, Proc. Natl. Acad. Sci. 115, 1227(2018).
46. Suguru Hosoi, Kohei Matsuura, Kousuke Ishida, Hao Wang, Yuta Mizukami, Tatsuya Watashige, Shigeru Kasahara, Yuji Matsuda, and Takasada Shibauchi, Proc. Natl. Acad. Sci. 113, 8139 (2016).