Local structure and Fe-vacancy disorder to order crossover in K$_x$Fe$_{2-y}$Se$_{2-z}$S$_2$

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The detailed account of the local atomic structure and structural disorder at 5 K across the phase diagram of K$_x$Fe$_{2-y}$Se$_{2-z}$S$_2$ ($0 \leq z \leq 2$) high temperature superconductor is obtained from neutron total scattering and associated atomic pair distribution function (PDF) approach. Various model independent and model dependent aspects of the analysis reveal a high level of structural complexity on the nanometer length-scale. Evidence is found for considerable disorder in the c-axis stacking of the FeSe$_{1-z}$S$_z$ slabs, presumably associated with substoichiometric potassium intercalation. The faulting does not exhibit any noticeable S-content dependence. The diffraction data do not display observable signs of turbostratic character of the disorder. In contrast to non-intercalated FeSe parent superconductor, substantial Fe-vacancies are present in K$_x$Fe$_{2-y}$Se$_{2-z}$S$_z$ deemed detrimental for superconductivity when ordered. Our study suggests that distribution of vacancies significantly modifies the effective interatomic potentials which, in turn, affect the nearest neighbor environment, in agreement with observed evolution of the PDF signal. Complementary aspects of the data analysis imply existence of a cross-over like transition at around $z = 1$ from predominantly vacancy-disordered state at the selenium end to more vacancy-ordered state closer to the sulfur end of the diagram. The S-content dependent measures of the local structure are found to correlate well with the evolution of the electronic state, suggesting that local structure may play an important role in the observed electronic properties. The local structural measures do not evolve across the superconducting Tc in the Se endmember, and exhibit distinct behavior with S-content for $z < 1$ and $z > 1$. This behavior appears to be anti-correlated with the evolution of the Fe-vacancy distribution with S content, reinforcing the idea of the intimate relationship of Fe vacancies to the local structure and observed properties.

INTRODUCTION

The discovery of alkali metal-intercalated A$_x$Fe$_2$Se$_2$ (A = K, Rb, Cs or Tl) superconductors$^{[1,2]}$ with relatively high transition temperatures ($T_c \approx 31$ K) as compared to their non-intercalated FeSe counterpart$^3$ has placed them in the focus of interest in the condensed matter physics community. However, the exact crystal structure of these materials and what triggers the superconductivity remains an unresolved problem. Importantly, this class of unconventional superconductors combines unique behaviours that are not observed in other iron-based superconducting systems, such as the coexistence of superconductivity and a long-range antiferromagnetic (AF) order with a large magnetic moment and a Nel temperature above room temperature$^{[4,7]}$. Large number of detailed studies based on a wide range of experimental techniques, such as neutron$^8$ and high-resolution synchrotron X-ray$^9$ diffraction, Mössbauer spectroscopy$^{10}$, Raman scattering$^{11}$, scanning tunneling microscopy$^{12}$, scanning single-crystal X-ray diffraction$^{13}$ and transmission electron microscopy$^{14}$, have shown strong evidence for a nanoscale phase separation in order to describe as accurately as possible the crystal structure and explain the coexistence of superconducting and AF states.

The majority insulating AF I4/m Fe-vacancy-ordered A$_x$Fe$_4$Se$_5$ phase is separated from the minority superconducting I4/mmm phase A$_x$Fe$_2$Se$_2$[15]. The latter is characterized by fully occupied Fe atomic sites (Fig. [1]. However, the inhomogeneity and complexity of phase separation in A$_{1-x}$Fe$_{2-y}$Se$_{2-z}$ makes it difficult to derive definitive conclusions about the precise nature of the correlation between the atomic structure and the observed physical properties of the system. Our earlier neutron PDF study$^{[16]}$ of the K-intercalated iron selenide and iron sulfide analogues revealed that the two-phase mixture description, combining the insulating Fe-vacancy-ordered K$_2$Fe$_4$Ch$_5$ and the superconducting K$_x$Fe$_2$Ch$_2$ (Ch=Se, S) constituents, is on a sub-nanometer scale effectively equivalent with a Fe-vacancy-disordered I4/m K$_{2-x}$Fe$_{4+y}$Se$_5$ single phase picture. This comes about due to the fact that Fe vacancies have an unconstrained distribution in the disordered superstructure. The question therefore still remains on the exact role that the Fe vacancies play in the emergence or collapse of superconductivity.

Until recently, it was believed that the presence Fe vacancies, irrespective of ordering, in the insulating phase...
is detrimental for the superconductivity. However, an understanding is emerging that what makes the material non-superconducting is the magnetism bearing $\sqrt{5}\times\sqrt{5}$ long range ordering of Fe vacancies. This is described by a model with $I4/m$ symmetry that features two crystallographically distinct atomic sites, and Fe atoms selectively fully occupy one of them (16i), leaving the other (4d) completely empty. Wu et al. have suggested that the non-superconducting FeSe-based magnetic insulators, which possess such Fe-vacancy ordered structures, should be considered as parent compounds of these superconductors 17. Disordering the Fe vacancy order of the parent magnetic insulating phase, $K_2Fe_2Se_5$, has therefore been proposed to be the key for the emergence of superconductivity in $K_xFe_{2-y}Se_2$ 18. As revealed by Wang et al., the Fe-vacancy order to disorder transition can be achieved by applying a simple high-temperature annealing 19. Two X-ray absorption fine structure studies 20, 21 provided clear evidence for local disorder in the structure of superconducting $K_xFe_{2-y}Se_2$, based on which it was suggested that a non-zero population of Fe atoms at the 4$d$ site is a key structural parameter for the bulk superconductivity 21. Another recent study which combines high energy X-ray diffraction and Monte Carlo simulations, also suggests that superconductivity in quenched $K_xFe_{2-y}Se_2$ single crystals appears at the Fe-vacancy order-to-disorder boundary 22. The quenching conditions during sample synthesis also appear to have a significant impact on the superconductivity of FeSe-based compounds 23. Applying a higher cooling rate in the quenching process of single crystals of $Rb_xFe_{2-y}Se_2$ was found to yield specimens with a higher $T_c$. An in situ scanning electron microscopy study revealed that during the cooling to room temperature, the formation mechanism of superconducting phase in pseudo-single-crystal $K_xFe_{2-y}Se_2$ comes from an imperfect Fe-vacancy disorder-to-order transition, which is deemed responsible for the phase separation 24.

The reported phase diagram across the $K_xFe_{2-y}Se_{2-z}S_z$ (0 $\leq$ z $\leq$ 2) compositional series revealed that the substitution of Se by the isovalent S suppresses the superconducting state and eventually, for z $\geq$ 1.6, superconductivity collapses 15. The sulphide end-member, $K_xFe_{2-y}S_y$ exhibits a spin-glass behavior at temperatures below 32 K 25. While it is clear that the suppression of superconductivity across the $K_xFe_{2-y}Se_{2-z}S_z$ series is connected to structural details, the nature of this connection remains unclear due to a lack of local structure studies. With this motivation, we have used PDF to probe the local atomic structure that may affect this notable change in behavior on a dense grid of compositions. To that end, we carried out a systematic neutron total scattering study at 5 K, the temperature at which superconductivity is observed in the selenium dominated part of the phase diagram, and which gets suppressed towards the sulfur end of the series. We utilized neutron PDF analysis combined with simulations based on large atomistic models to explore subtle nano-scale changes in the interatomic distances and the evolution of vacancy distribution in the Fe layers in the $K_xFe_{2-y}Se_{2-z}S_z$ system. Based on these complementary analysis methods, evidence for Fe-vacancy disorder to order crossover around $z = 1$ composition is revealed, reinforcing the idea that the Fe-vacancy distribution is the key structural parameter affecting the properties. Our study further unmasks
so far unreported, yet not unexpected, disorder in the stacking of the FeSe$_{1-x}$S$_x$ slabs in this intercalated superconducting system, which reflects an additional component in an already structurally complex material.

**METHODS**

**Sample synthesis** – Single crystals of K$_x$Fe$_{2-y}$Se$_{2-z}$S$_z$ ($0 \leq z \leq 2$) were grown by self-flux method, as described in detail elsewhere [25], and pulverized into fine powders. Samples were thoroughly characterized by X-ray powder diffraction, magnetic susceptibility, and electrical resistivity measurements, as previously reported [15].

**Neutron total scattering** – Experiments were performed at NOMAD instrument [26] at the Spallation Neutron Source at Oak Ridge National Laboratory. Eleven finely pulverized samples, 0.5 g of each, equally spaced across the Se/S compositional space ($\Delta z = 0.1$), were loaded into 6 mm diameter extruded vanadium containers under inert atmosphere and sealed. Helium was used as the exchange gas. Each sample was mounted in the diffractometer equipped with Orange cryostat. The instrument was calibrated using diamond powder standard. Powder diffraction data were collected after thorough equilibration at 5 K for 2 h of total counting time for each sample. Data correction and reduction followed standard protocols [27]. Neutron PDFs were obtained via Sine Fourier transforms of the measured reduced total scattering functions $F(Q)$, where $Q$ is the momentum transfer, over a range from $Q_{\text{min}} = 0.5$ Å$^{-1}$ to $Q_{\text{max}} = 26$ Å$^{-1}$, using the PDFGui program [28].

**PDF peak analysis** – Fitting of PDF data for decomposition into constituent peaks was done with the fitpy v 1.3.1 software package [25] using Gaussian functions and a linear baseline function where the intercept term was fixed at zero.

$F(Q)$ diffuse signal fitting – The $F(Q)$ data of each samples were fitted with a damped sine function after subtracting a fitted linear background.

**Structural models** – Within the system, two possible structural models have been put forward. The simplest model, with space-group $I4/mmm$, consists of FeCh (Ch = Se/S) slabs featuring a Fe square planar sublattice. Each Fe is coordinated by four Ch creating layers of edge-shared FeCh$_4$-tetrahedra, stacked along the c lattice direction and interleaved with K species equidistant from each layer. In this model, the asymmetric unit contains a single Fe at $4d$ (0.0, 0.5, 0.25), Ch at $4e$ (0.0, 0.0, 0.0), and K at $2a$ (0.0, 0.0, 0.0). The relatively simple structure, with only one unique Fe site, gives little flexibility for handling vacancies on the Fe sub-lattice, which are common in this system [17].

A more complicated model, with space-group $I4/m$, is related to the higher symmetry $I4/mmm$ model through a rotation in the a – b plane and a $\sqrt{2}$ increase in the a = b lattice parameters. The increase in unit cell size doubles the number of atoms in the asymmetric unit, with two symmetrically distinct Fe at $4d$ (0.0, 0.5, 0.25) and 16$i$ (x, y, z), Ch at $4e$ (0.0, 0.0, 0.0), and K at $2b$ (0.0, 0.0, 0.5) and 8$h$ (x, y, 0.5). Importantly, within both these symmetries the FeCh$_4$-tetrahedra of adjacent layers are translated in the x and y direction by half unit cell lengths. This can be contrasted with the related, non-K intercalated FeCh group of superconductors, where adjacent layers of FeCh$_4$-tetrahedra contain no such relative x and y translation.

**Small-box refinements** – The experimental PDF data were fit with the structural models described over a 10 Å range using the PDFGui software [29]. Over wider $r$-ranges the experimental PDF is dominated by the interlayer correlations, and our analysis reveals that these are dominated by appreciable stacking disorder, which is highly non-trivial to handle using conventional PDF approaches and is beyond the scope of this study. Two
alternative modeling approaches were attempted in subnanometer regime. First approach used a mixture of stoichiometric $I4/mmm$ and fully Fe-vacancy ordered (VO) $I4/m$ phase components. Second approach utilized vacancy disordered (VD) version of $I4/m$. The two approaches were found to yield effectively identical fit qualities and comparable descriptions of the underlying structure [16]. For simplicity, only the VD model with $I4/m$ symmetry was systematically applied to all the data using a total of 19 fitting parameters. These included the unit cell parameters ($a = b \neq c$), a scale factor, and a correlated motion parameter $\delta_1$ [30]. Further, the fractional coordinates were refined according to the space group constraints (9 parameters), and the atomic displacement parameters (ADP) were set to be isotropic $(u_{11} = u_{22} = u_{33})$ and identical for all atomic species of the same type (3 parameters). The occupancies of the two symmetry-distinct Fe crystallographic sites ($4d$ and $16i$) were allowed to vary separately, while the occupancies of potassium atoms in $2b$ and $8h$ sites were constrained to be equal because of relative insensitivity of the neutron PDF to potassium (3 occupancy parameters). The occupancies of Ch species were fixed at their nominal values as refinements did not suggest local segregation to the two symmetry-distinct sites. Refinements were done sequentially, such that for any given composition the PDF refinement was initialized using the converged model of the previous composition.

Large-box simulations – Simulated PDFs were computed with aid of the DISCUS v 5.30.0 software package [31] using a model with space group $I4/m$. The global concentration of Fe was fixed at 80%, with 100% occupancy of the $16i$ site and 0% occupancy of the $4d$ site. The global concentration of K was fixed at 80%, spread evenly across the $2b$ and $8h$ sites. For stacking fault simulations, the stack module of the DISCUS software package was used, with a layer supercell of $2 \times 2$ unit cells and total thickness of 1,500 layers. The powder pattern was computed using the Fast Fourier method in DISCUS, with a 0.001 reciprocal length unit (r.l.u) mesh for powder integration. For simulations on the impact of vacancy disorder, a supercell of $50 \times 50 \times 1$ unit cells was used. Atoms were initialized with a random thermal displacement such that their mean squared displacement across the whole supercell was consistent with the ADP parameters refined from the $K_xFe_{2-y}S_{2-z}S_z$ PDF data. Following this, atomic displacement vectors were swapped between atoms of like identity to minimize the total energy composed of a pairwise Lennard Jones (LJ) potential between nearest neighbor (NN) Fe-Ch pairs. The LJ potential was constructed such that the equilibrium NN Fe-Ch bond distance was that refined from the $K_xFe_{2-y}S_{2-z}S_z$ PDF data. Swaps were always accepted if they decreased the total energy, and conditionally accepted if they increased the total energy, with probability $p = \exp (-\Delta E/kT)$, where $\Delta E$ is the change in energy associated with the swap, $k$ is the Boltzmann constant, and $T$ is the temperature, in this case 5 K. The total number of swaps was fixed at 100 times the number of atoms in the supercell.

RESULTS AND DISCUSSION

Neutron diffraction – Neutron diffraction data across the entire composition series show a broad and bi-modal distribution of intensity in the expected location of the (002) peak. An example of this is shown for $K_xFe_{2-y}S_2$ in Fig. 2, where the primary (002) peak is expected at $\sim 0.95$ Å$^{-1}$, and no feature is expected at $\sim 0.8$ Å$^{-1}$, based on either the $I4/mmm$ or the $I4/m$ model. This is a feature commonly seen in clay systems with layered structures and variable inter-layer distances [32,34]. DISCUS simulations considering large super-cells of the $K_xFe_{2-y}S_2$ system with two distinct inter-layer distances, 6.5 Å (93% prevalence) and 8.0 Å (75% prevalence) (see Fig. 3b) reproduce this bi-modal intensity distribution well, as seen in Fig. 3b. Similar DISCUS simulations with a single inter-layer distances but random shifts along the $a$ and $b$ lattice directions (see Fig. 3d) produce a diffraction pattern characteristic for a turbostratic material, where $hkl$ peaks are broadened into indistinct $hk$-bands [34,35]. As can be seen in Fig. 3d, this significantly reduces the number of distinct Bragg peaks, and creates a characteristic saw-tooth pattern. In Fig. 3f we again present an example diffraction pattern for $K_xFe_{2-y}S_2$, where no such saw-tooth like features are observed. These simulations demonstrate the $K_xFe_{2-y}S_{2-z}S_z$ series exhibits at least two distinct inter-layer distances,
without turbostratic disorder. This anisotropic crystallinity naturally suppresses inter-layer correlations, while intra-layer correlations persist. For this reason, our small-box PDF modelling is limited to the very local structure ($r < 10$ Å).

Reduced total scattering structure functions $F(Q)$ for the $K_xFe_{2−y}Se_2$ and $K_xFe_{2−y}S_2$ end-members are shown in Fig. 3a and Fig. 3b, respectively, along with the related FeSe compound in Fig. 3c. It is clear when viewing this series that Bragg peaks at high-$Q$ are suppressed when moving from the sulfur to the selenium end-member. This is especially true when compared to the FeSe compound without K-intercalation. Suppression of Bragg peaks is a clear indicator for the presence of disorder, suggesting that disorder increases when moving from the FeSe “parent” non-intercalated phase to $K_xFe_{2−y}S_2$ and again when moving to $K_xFe_{2−y}Se_2$.

The diffuse signal in $F(Q)$ for the entire $K_xFe_{2−y}Se_{2−z}S_z$ series, shown in Fig. 3d, also has a sinusoidal behavior at high-$Q$. Fitting with a damped Sine function in the range $12 \leq Q \leq 25$ Å$^{-1}$ allows us to extract the amplitude and frequency of this oscillation as a function of sulfur content $z$, shown in Fig. 3e and Fig. 4a. We note that these oscillations are the strongest in the selenium end-member, and are gradually suppressed with increasing sulfur content, reaching a minimum in the range $1.2 \leq z \leq 1.6$. Above $z = 1.6$, these oscillations again increase in amplitude. This suppression and recovery is highlighted when viewing the fitted Sine functions, as can be seen in Fig. 4b and Fig. 4c.

**FIG. 4.** (Color online) Analysis of the diffuse scattering signal in $F(Q)$ at high-$Q$ in $K_xFe_{2−y}Se_{2−z}S_z$. (a) The measured (lighter line) and fitted (heavier line) $F(Q)$ signal. The curves are sequentially offset vertically by 2 Å$^{-2}$ for clarity. (b) The model $F(Q)$ signal over a regime of concentrations where the oscillation amplitude and frequency decrease. (c) The model $F(Q)$ signal over a regime of concentrations where oscillation amplitude and frequency increase. (d) The amplitude of $F(Q)$ diffuse oscillations as a function of sulfur content, $z$. (e) The frequency of diffuse oscillations as a function of $z$. Colors represent sulfur content, $z$, as indicated, and in (b) and (c) are consistent with those in (a).

**FIG. 5.** (Color online) PDF data of the $K_xFe_{2−y}Se_{2−z}S_z$ series at 5 K. (a) The experimental PDFs in the local structure range $1.5 \leq r \leq 8$ Å. The sulfur and selenium end-members are shown with a blue and red line, respectively, while intermediate compositions are shown in gray. Inset is a false color map representation of the same PDF data plotted vs $r$ and $z$, highlighting the relative lack of change in the position of the first PDF peak at $r \approx 2.48$ Å as a function of sulfur content until approximately $z = 1$. The peak starts evolving for higher $z$ values. (b) A plot of the peak position of the feature marked by an orange arrow in (a) as a function of sulfur content $z$. A dashed line is a guide to the eye, included to highlight the nearly linear behavior of this peak position with $z$. (c) A plot of the Fe-Ch peak position, marked by a blue arrow in (a), as a function of $z$. Two dashed lines are guides to the eye, highlighting the two-regimes behavior.

**PDF analysis –** Interpretation of these Sine-like oscillations of the diffuse signal in $Q$-space is not straightforward. However, the presence of a sinusoidal oscillation in $F(Q)$ should map to the PDF $G(r)$, as the two are related by a Fourier transform. Specifically, a periodic signal in $F(Q)$ with frequency $f$ and amplitude $A$ should manifest as an enhancement (proportional to $A$) of the peak in $G(r)$ at $r = 2\pi f$.

Indeed, this agrees with qualitative assessments of the PDFs. The frequency and relative amplitude of the periodic signal in $F(Q)$ parallels the position and relative sharpness (compared to higher-$r$ peaks) of the first PDF peak. In $K_xFe_{2−y}Se_2$, the PDF (Fig. 3a) shows a sharp peak at $r \approx 2.43$ Å, followed by relatively broad features at higher-$r$. Conversely, the PDF of $K_xFe_{2−y}S_2$, shown in Fig. 3b, shows a peak at $r \approx 2.38$ Å which is of comparable breadth to high-$r$ peaks.

Typically, the observation of $r$-dependent PDF peak widths is associated with correlated atomic motion [30]. Generally speaking, these relative widths describe the nature of the bonding in the material [30].

The observed PDFs at 5 K are shown in Fig. 3a, and the positions of the first peak, representing Fe-Ch correlations, as well as a higher-$r$ peak are shown in Fig. 3b.
FIG. 6. (Color online) Fits of the structural models to the PDF data. The fit to the observed K$_x$Fe$_{2-y}$Se$_2$ PDF data using either: (a) a single-phase $I4/m$ vacancy disordered (VD) model or (b) a two-phase model with $I4/m$ vacancy ordered (VO) and $I4/mmm$ components. Similar one- and two-phase fits are shown in (c) and (d), respectively, for the K$_x$Fe$_{2-y}$S$_2$ PDF data. In various panels arrows point to intracluster and intercluster Fe-Fe PDF peaks, as indicated. See text and Fig. 5 for details. In all cases, fits were over the displayed r-range (1.5 $\leq$ r $\leq$ 10 Å). PDF data and fits are shown with open circles and solid red lines, respectively, and the difference curves (solid green lines) are shown offset vertically for clarity. Inset in (c) summarizes the single-phase PDF refinement derived evolution with sulfur content of Fe occupancy of the two distinct Fe sites (4d and 16i) in the $I4/m$ VD model. A vertical dashed line represents the two-regimes boundary discussed in the text.

and Fig. 5c, respectively. Interestingly, the position of the first (Fe-Ch) peak is nearly unchanged in the range 0.0 $\leq$ z $\leq$ 1.0, signifying that the Fe-Ch pair distance is unaffected by the substitution of sulfur for selenium. This in stark contrast to the typical Vegard’s law-type behavior, predicting a linear change in lattice parameter as a function of chemical substitution due to steric effects [37]. Indeed, this linear change is recovered if we consider the position of most higher-r peaks (Fig. 5a and 5b), indicating that the very local structure has a distinct behavior.

Fitting the local structure region of the observed PDFs (1.75 $\leq$ r $\leq$ 10 Å) with a two-phase model incorporating both the vacancy ordered $I4/m$ model and the $I4/mmm$ model yielded fits which were equivalent to those done with a single-phase vacancy disordered $I4/m$ model. Examples of these fits for the S- and Se-end-members are shown in Fig. 6. Importantly, only the lower symmetry $I4/m$ model supports the existence of two unique Fe-Fe correlation peaks representing inter- and intracluster Fe-Fe correlations (see Fig. 1 and Fig. 6). For these reasons, the single-phase vacancy disordered $I4/m$ model was preferred and utilized here.

The inset in Fig. 6: shows the refined occupancy of the two symmetrically distinct Fe sites, at 4d and 16i. As sulfur is substituted for selenium, the 4d site moves from partially occupied to completely empty, whereas the 16i site moves from partially vacant to completely occupied. The situation where the 4d Fe is completely vacant and the 16i is completely occupied represents the vacancy-ordered phase, associated with suppression of superconductivity [17], whereas a uniformly vacancy disordered phase is recovered when both sites have near identical occupancies. Thus, we note a cross-over behavior in the vacancy ordering of the local structure. According to our PDF fits, this transition occurs in this system at z = 1.0, or about 50 % sulfur substitution at 5 K.

These results again suggest a two-regime behavior of K$_x$Fe$_{2-y}$Se$_{2-z}$S$_z$ in composition-space, consistent with the electronic properties (Fig. 1) at 5 K, our analysis of the $F(Q)$ (Fig. 1), and our model-independent analysis of the PDF (Fig. 5).

While each aspect of our analysis highlights that the K$_x$Fe$_{2-y}$Se$_{2-z}$S$_z$ series exhibits a two-regime behavior at 5 K, it is not immediately apparent how each aspect is connected. Electronic transport (Fig. 1) measurements suggest that $T_c$ is suppressed beginning at z = 1.0, with no evidence of superconductivity above z $\approx$ 1.5. The structure function $F(Q)$ shows high-Q oscillations which decrease in magnitude and frequency up to z = 1.6 and then recover for z > 1.6 (Figs. 5 and 6).
The frequency and magnitude of these \( F(Q) \) oscillations correlate with the position and relative sharpness, respectively, of the Fe-Ch NN peak as observed in the PDFs of the \( K_x\text{Fe}_{2-y}\text{Se}_{2-z}\text{S}_z \) series at 5 K. Both the \( F(Q) \) and \( G(r) \) results demonstrate that this Fe-Ch NN peak obeys Vegard’s law up to about \( z = 1.0 \). The exaggerated sharpness of this Fe-Ch NN peak (relative to higher-\( r \) PDF peaks) in the selenium rich \(( z < 1.0 )\) regime signifies that the Fe-Ch bond length distribution (BLD) is significantly narrower compared to Fe-Ch BLD in the sulfur rich \(( z > 1.0 )\) regime \( [16] \). This Fe-Ch BLD in \( K_x\text{Fe}_{2-y}\text{Se}_2 \) (Fig. 5) is also much sharper even than that seen in FeSe, observed under similar conditions (Fig. 5). This is interesting, as both \( K_x\text{Fe}_{2-y}\text{Se}_2 \) and FeSe are composed locally of the same structural motif of \( \text{FeSe}_4 \) edge-shared tetrahedra, and thus the observed differences in the two Fe-Se BLDs are not due to simple steric effects. It is then also possible that something other than simple steric differences between sulfur and selenium contribute to the differences in relative Fe-Ch BLDs (peak sharpness) across the \( K_x\text{Fe}_{2-y}\text{Se}_{2-z}\text{S}_z \) series.

Importantly, the PDF fitting results (Fig. 4) suggest that the two regime behavior is marked by a crossover at \( z = 1.0 \) from a partial \(( z < 1.0 )\) to complete \(( z > 1.0 )\) vacancy-order within the local structure. While it is expected that vacancy ordering impacts the overall disorder of the structure, it is also possible that it directly impacts the Fe-Ch BLD. To test this hypothesis, we considered two large atomistic models, one with a completely ordered arrangement of vacancies (Fig. 7a) and the other with a uniformly disordered arrangement of vacancies (Fig. 7d). Importantly, these two configurations had identical overall vacancy concentrations (20 %).

In these atomic configurations, each chalcogen species can potentially be coordinated by up to four iron species, or up to four vacancies. For each atomistic model, we quantified the total number of each of the five possible configurations. These results are presented in Fig. 7a,d for the vacancy-ordered and -disordered atomistic model, respectively. For the vacancy-ordered case, the results are as expected, 20 % of chalcogenes are fully coordinated by four iron, whereas 80 % of chalcogenes are coordinated by three iron and a single vacancy. In the vacancy-ordered case there are no chalcogenes coordinated by two or more vacancies.

The vacancy-disordered case is more interesting: a significant fraction \(( \sim 20 \%)\) are severely under-coordinated, with two or more missing iron NN. Moreover, the percentage of fully coordinated chalcogenes nearly doubles in the vacancy-disordered case. These configurations are associated with the superconducting \( I4/mmm \) phase devoid of vacancies \( [16] \). Surprisingly, the increase in fully coordinated chalcogenes is a result of disordering the vacancies in this system. This supports but also possibly explains the results of previous studies where annealing to induce Fe-vacancy disorder led to superconductivity \( [17] \).

Further, if the two configurations exemplified by Fig. 7a,c are energy minimized in the presence of an identical LJ potential between Fe and Ch NNs, the resulting NN BLDs, shown in Fig. 7, are different. Specifically, the Fe-Ch BLD of the energy minimized vacancy-disordered configuration is noticeably sharper than the vacancy-ordered configuration. This is surprising, given that the sharper distribution originates from a system with more overall disorder.

This demonstrates that relative arrangement of vacancies has an intrinsic impact on the Fe-Ch BLD, all other things being equal. This makes intuitive sense, as the vacancy-disordered state shows a greater prevalence of severely undercoordinated chalcogen species. It is reasonable to assert that these severely undercoordinated chalcogenes will bind more strongly with the fewer iron species they are coordinated by, leading to a relatively narrower Fe-Ch BLD.

The result also offers an explanation of the two-regime behavior, specifically that for \( z < 0.50 \) (selenium-rich) the local structure is partially vacancy-disordered. This disorder manifests in \( F(Q) \) through suppression of Bragg peaks at high-\( Q \) (Fig. 3), leading to the observation of a strong sinusoidal intensity oscillation. In \( G(r) \) this oscillation manifests as a relatively sharp first peak followed by broader high-\( r \) peaks (Fig. 3), corresponding to a well defined Fe-Ch BLD.

**CONCLUSIONS**

In summary, the local atomic structure and structural disorder have been characterized across the phase diagram of \( K_x\text{Fe}_{2-y}\text{Se}_{2-z}\text{S}_z \) \(( 0 \leq z \leq 2 )\) system, displaying both superconductivity and magnetism, by means of neutron total scattering and associated atomic PDF analysis of 5 K data. Using various model independent and model dependent approaches we find a high level of structural complexity on the nanometer length-scale. Through simulations based on large scale atomistic models we demonstrate that the distribution of vacancies significantly modifies the effective interatomic potentials, observably affecting the nearest neighbor environment, as corroborated by the features in the data. Complementary aspects of the analysis reveal a crossover like behavior, with an onset at \( z \approx 1 \), from predominantly vacancy-disordered state towards the selenium end of the phase diagram, to a more ordered vacancy distribution closer to the sulfur end of the diagram. The evolution of the local structure with sulfur content displays apparent correlation with the changes seen in the electronic state, emphasizing the importance of the local structure for the observed electronic properties. The results demonstrate the direct impact of the Fe-vacancy distribution.
on the local structure, and reinforce the idea of its critical influence on superconductivity. Finally, the analysis also highlights the presence of considerable disorder in the c-axis stacking of the FeSe$_1_{x}$S$_x$ slabs, which has a non-turbostratic character and appears independent of S-content.

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