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Friedel-like Oscillations from Interstitial Iron in Superconducting $\text{Fe}_{1+y}\text{Te}_{0.62}\text{Se}_{0.38}$

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Using polarized and unpolarized neutron scattering we show that interstitial Fe in superconducting $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ induces a magnetic Friedel-like oscillation that diffracts at $\mathbf{Q}_\perp = (\frac{1}{2}, 0)$ and involves > 50 neighboring Fe sites. The interstitial $> 2 \mu_B$ moment is surrounded by compensating ferromagnetic four spin clusters that may seed double stripe ordering in Fe_{1+y}Te . A semi-metallic 5-band model with $(\frac{1}{2}, \frac{1}{2})$ Fermi surface nesting and four fold symmetric super-exchange between interstitial Fe and two in-plane nearest neighbors largely accounts for the observed diffraction.

While superconducting $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ shares band structure, Fermi surface [1], and a spin resonance [2] with Fe pnictide superconductors [3–5], the parent magnetic structures are surprisingly different. Fig. 1(a) depicts the distinct magnetic unit cells with single striped order for 122 arsenides ($\mathbf{q}_m = (\frac{1}{2}, \frac{1}{2})$) [6] versus double stripes for Fe_{1+y}Te ($\mathbf{q}_m = (\frac{1}{2}, 0)$) [7, 8]. In this letter we show that short range ordered glassy magnetism at $(\frac{1}{2}, 0)$ in superconducting $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ ($x = 0.38$) arises from magnetic Friedel-like oscillations surrounding interstitial Fe forming what we call a magnetic polaron. A critical role of interstitial iron to stabilize the lamellar structure [9], enhance magnetism [10], and reduce the superconducting volume fraction [11] was previously noted. Our results provide a quantitative microscopic view of the pivotal magnetic polaron.

We used three co-aligned $\text{Fe}_{1+y}\text{Te}_{0.62}\text{Se}_{0.38}$ single crystals with total mass ≈ 20 g and $y = 0.01(2)$ determined by EDX. Grown by a flux method [11], the samples are tetragonal (space group $P4/nmm$) with low temperature (T) lattice parameters $a = 3.791 \text{ \AA}$ and $c = 6.023 \text{ \AA}$. Magnetization and specific heat measurements yielded $T_c = 14.0(2) \text{ K}$ and a superconducting volume fraction of 92.9(7)% and 83(1)% respectively (Fig. 5(b)).

Neutron scattering was performed using the Multi Axis Crystal Spectrometer (MACS) at NCNR [12]. Twenty detection channels permitted mapping of elastic scattering throughout a reciprocal lattice plane [13]. High T measurements ($T = 25 \text{ K}$) provided background to cancel the dominant elastic nuclear scattering so the difference data probe magnetic correlations that become static below 25 K. Polarized neutrons were used to establish the magnetic origin and polarization of the scattering. Spin polarized ^3He gas held in glass cells within a vertical solenoid concentric with the sample rotation

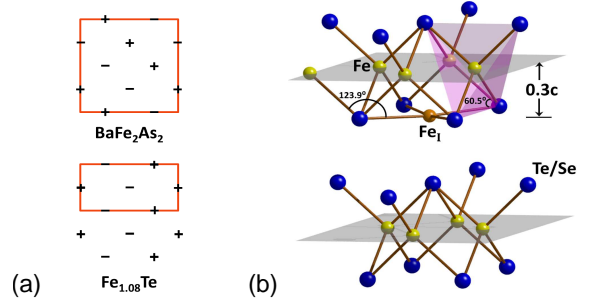


FIG. 1. (a) Fe-plane magnetic order in the 122 and 11 parent compounds. (b) Half unit cell of $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ showing the location of interstitial Fe in orange (Fe_I).

axis was used to select the vertical component of neutron spin before and after detected scattering events [14]. The 5 meV flipping ratio was typically 56 and 8.4 for Bragg scattering from Al_2O_3 and $\text{Fe}_{1+y}\text{Te}_{0.62}\text{Se}_{0.38}$ respectively. The corresponding sample depolarization factor of 0.825 was T -independent between 4 K and 30 K. A channel mixing correction, obtained from the measured flipping ratio, and transmission correction for time dependent ^3He polarization ($\tau \approx 60 - 90$ hours) - averaging 60 (42) for the non-spin-flip (spin-flip) channel - was applied to T -difference data. The measurement protocol ensured less than 5% effect of varying cell transmission on T -difference data. Absolute normalization of the unpolarized scattering cross section was obtained through comparison to acoustic phonon scattering and checked against incoherent elastic scattering from vanadium. The polarized beam configuration was calibrated to the unpolarized configuration through incoherent elastic scattering from the sample.

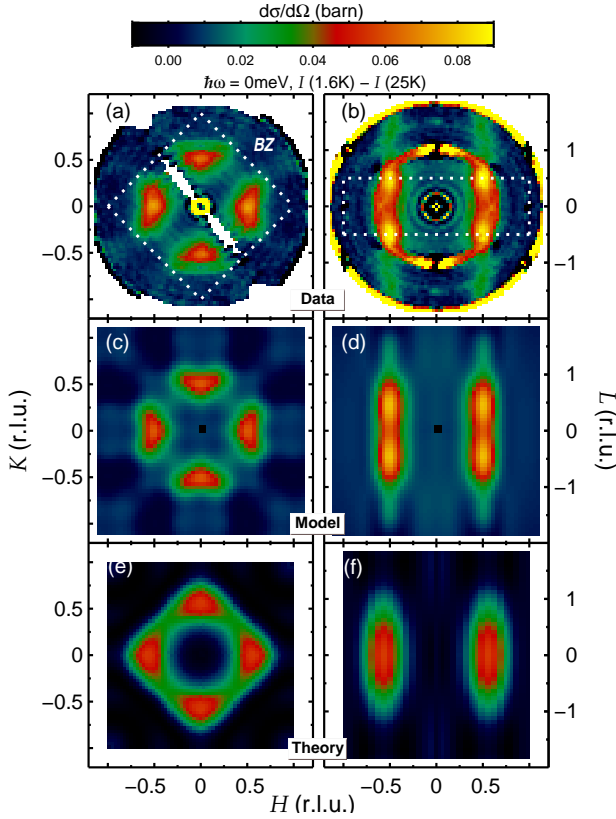


FIG. 2. (a) Constant $\hbar\omega = 0$ slice showing the difference between neutron scattering intensity, I , at $T = 1.6$ K and $T = 25$ K in the $(HK0)$ and (b) $(H0L)$ scattering planes with $E_i = E_f = 3.6$ meV. The data were measured with sample rotation about a vertical axis spanning 90 degrees. With the assumption that $I(\mathbf{Q}) = I(-\mathbf{Q})$, the figures show $(I(\mathbf{Q}) + I(-\mathbf{Q}))/2$. Features near the origin, $(0, 0, \pm 1)$ Bragg peaks, and around the perimeter in (b) arise from intense nuclear scattering. (c)-(d) Calculated intensity distribution for a 4-fold symmetric spin cluster surrounding interstitial Fe. (e)-(f) Calculated intensity for an interstitial Fe-site exchange coupled to a five d-orbital model.

Fig. 2(a)-(b) show the wave vector dependence of the difference between elastic scattering at $T = 1.6$ K and $T = 25$ K. The rod like nature of scattering in the $(H0L)$ plane (Fig. 2(b)) indicates quasi-2D correlations. Neglecting the interstitial site, $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ has only one Fe site per primitive unit cell. The wave vector dependence of magnetic neutron scattering associated with the periodic structure therefore must repeat in each Brillouin zone. This implies - modulo the magnetic form factor and polarization factor - that the intensity for $L = \pm\frac{3}{2}$ should match that at $L = \pm\frac{1}{2}$. A possible explanation for the reduced intensity at $L = \pm\frac{3}{2}$ (Fig. 2(b)) is an uniaxial spin configuration $\parallel \mathbf{c}$, which would imply that magnetic scattering would be exclusively non-spin-flip when neutron polarization $\mathbf{P} \parallel \mathbf{c}$ [15, 16].

Fig. 3 shows energy integrated T -difference scattering versus $\mathbf{Q} = (0.535, k, 0)$ for $\mathbf{P} \parallel \mathbf{c}$. The peak in the spin-

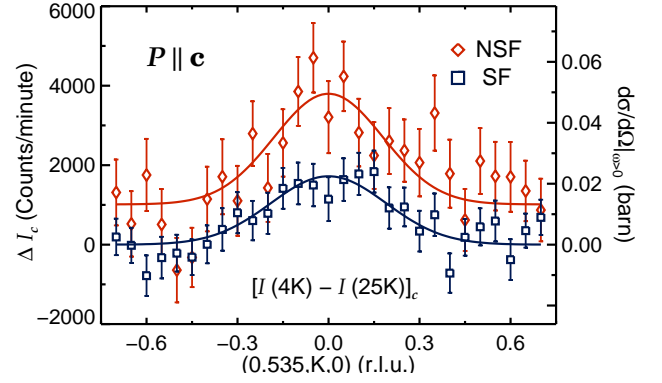


FIG. 3. Polarized neutron scattering measured along $\mathbf{Q} = (0.535, K, 0)$. $\Delta I_c = [I(4\text{ K}) - I(25\text{ K})]_c$ is the T -difference intensity without energy analysis following ^3He cell transmission correction. Red open diamonds are non-spin-flip data and blue open squares are spin flip data. The 1.4 mT guide field was perpendicular to \mathbf{Q} and parallel to \mathbf{c} . The reduction in the magnitude of the SF+NSF cross section without final energy analysis (≈ 0.06 barn) compared to the energy resolved unpolarized data (≈ 0.07 barn, Fig. 2a) is consistent with expectations for frozen spin systems [19]. Here and throughout the paper, error bars indicate \pm one standard deviation.

flip channel proves *that* part of the scattering cross section is magnetic. Assuming the non-spin-flip T -difference intensity is also magnetic, the intensity ratio of 0.67(12) between the spin-flip and non-spin-flip channels, implies that same ratio between the in- and out-of-plane components of the spin correlation function [16]. This ratio is too large for the corresponding polarization factor to account for the reduced intensity at $L = \pm\frac{3}{2}$. Likewise, in the $(HK0)$ plane the elastic magnetic scattering, which comprises four triangle shaped features at $(\pm\frac{1}{2}, 0)$ and $(0, \pm\frac{1}{2})$, is strongly suppressed in the adjoining Brillouin zones (Fig. 2(a)).

Because the calculated polarization and form factors for magnetic neutron scattering cannot account for the reduced intensities, we are led to conclude the real space features that give rise to this scattering do not carry the periodicity of the underlying crystal structure. Four fold rotation symmetry is however observed. These facts suggest the involvement of an aperiodic interstitial site. The interstitial Fe_I site (Fig. 1(b)) is located at the center of the primitive square Fe planar unit cell at roughly the same distance $d = zc$ from the Fe plane as the Te(Se) atoms ($z \approx 0.30(3)$) [17, 18].

Because of the so-called phase problem and to take into account other knowledge of the chemical structure, we use least squares fitting rather than a direct Fourier transform to obtain the real space spin configuration from the diffuse scattering. The parameters are magnetic dipole moments for the interstitial site and a total of 11 non-equivalent surrounding sites in each of the two planes sandwiching the interstitial. Since there is insufficient information for separate determination of spin con-

figurations in these two planes, the number of free parameters is reduced by forcing identical spin configurations in both planes allowing them to differ only by an attenuation factor, η , to account for weaker coupling to the more distant plane. Ordered by distance from the interstitial site, the distinct dipole moments in the near plane are denoted m_n , where $n = 1, 2, 3, \dots, 11$. The corresponding displacement vectors from the interstitial site are labeled \mathbf{r}_{nj} , where j indexes symmetry related sites. The parameters are inferred by minimizing the least squared deviation between the corresponding scattering function: $\mathcal{S}(\mathbf{Q}) \propto |m_0 + \sum_{nj} m_n \exp(i\mathbf{Q} \cdot \mathbf{r}_{nj})(1 + \eta \exp(i\mathbf{Q} \cdot \mathbf{c}))|^2$ and the observed wave-vector dependent T -difference intensity in the $(HK0)$ and $(H0L)$ planes. Here m_0 is the interstitial dipole moment.

The best fit $\mathcal{S}(\mathbf{Q})$ is shown in Fig. 2(c)-(d). That we are able to reproduce diffraction throughout the $(HK0)$ and $(H0L)$ planes with a value of $z = 0.23(6)$ consistent with structural data, and $\eta = -0.16(9)$ indicating antiferromagnetic correlation between adjacent planes, confirms interstitial magnetism. The inferred spin configuration is depicted in Fig. 4(a). The interstitial dipole moment is indicated by the central yellow dot and the surrounding moments are represented by yellow/blue dots (parallel/anti-parallel with m_0) - their magnitude proportional to the area of the dots. We see the nearest neighbor (NN) moments are parallel to the interstitial Fe moment. This is consistent with the acute Fe-Te(Se)-Fe_I bond angle (60.5° , Fig. 1(b)), which is expected to yield ferromagnetic (FM) superexchange [20]. Next nearest neighbors (NNN) on the other hand are antiparallel to the interstitial moment as expected for the obtuse (123.9°) Fe-Te(Se)-Fe_I bond angle. Comparison to atomic displacement discovered through diffuse x-ray scattering from Fe_{1+y}Te [21] shows FM (AFM) correlated spins are repelled (attracted), which is consistent with magneto-elastic displacements that enhance magnetic exchange interactions. FM square plaquettes seen along the diagonal direction in Fig. 4(a) are a resilient feature of magnetism in the 11 series that has also been noted in Fe_{1.1}Te [22] and Fe-vacancy ordered K_yFe_{2-x}Se₂ [23].

We also adjusted an overall spin space anisotropy parameter resulting in a ratio of $0.81(13)$ between \mathcal{S}^\perp and \mathcal{S}^{zz} . Consistency with the polarized beam value of $0.67(12)$ affirms the elastic T -difference scattering is magnetic. Absolute normalization of the intensity data further allows extracting $ym_0^2 = 0.22(3) \mu_B^2$. Note that this represents a lower bound on frozen moment because this results from a temperature difference measurement. For comparison the product of the nominal and EDX determined interstitial density and the squared free ion dipole moment of Fe³⁺, $m_0 = 5 \mu_B$, consistently yields $ym_0^2 = 0.25 \mu_B^2$.

The interstitial together with the two nearest neighbors is sufficient to reproduce the major features observed in the $(HK0)$ and the $(H0L)$ scattering planes. The finer details of Fig. 2(c) however, are obtained only when mo-

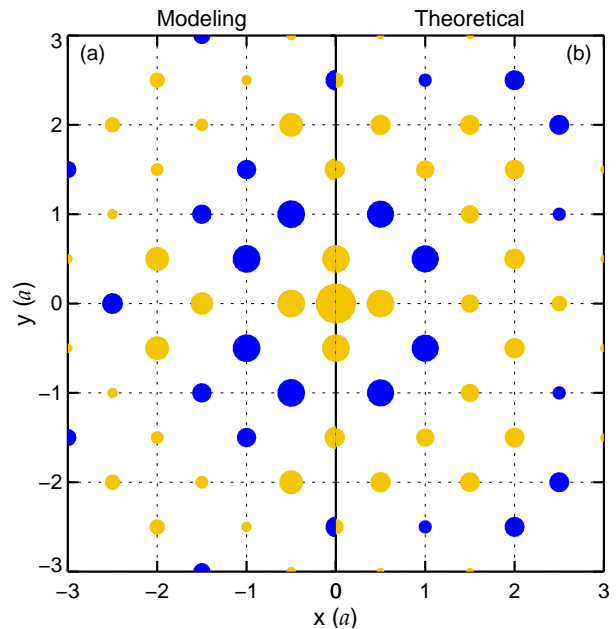


FIG. 4. Magnetic cluster in nearest neighbor Fe plane surrounding interstitial Fe: (a) inferred from the observed diffuse scattering pattern in Fig. 2 and (b) calculated from a five band theoretical model. Yellow (blue) moments are parallel (antiparallel) to the interstitial and the dot areas are proportional to the moment sizes.

ments beyond reach of direct superexchange interactions are included in $\mathcal{S}(\mathbf{Q})$. These display an oscillatory behavior reminiscent of a Friedel oscillation. For a more rigorous analysis that links the oscillatory magnetism to the Fermi surface structure of itinerant electrons as for the charge density in Friedel oscillations, we use a five band model with exchange interactions to the two nearest Fe spins. The Hamiltonian consists of three terms:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{imp}}, \quad (1)$$

where \mathcal{H}_0 describes the band structure within the five d -orbital model and \mathcal{H}_{int} includes the intra- (inter-) orbital repulsion U (U'), Hund coupling J_H , and inter-orbital pair-hopping, G_2 [24, 25]:

$$\begin{aligned} \mathcal{H}_{\text{int}} = & U \sum_{i,\mu} \hat{n}_{i\mu\uparrow} \hat{n}_{i\mu\downarrow} + \frac{U'}{2} \sum_{\substack{i,\mu \neq \nu \\ \sigma, \sigma'}} \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma'} - \\ & J_H \sum_{i,\mu \neq \nu} \mathbf{S}_{i\mu} \cdot \mathbf{S}_{i\nu} + \frac{G_2}{2} \sum_{\substack{\mu \neq \nu \\ \sigma \neq \sigma'}} f_{i\mu\sigma}^\dagger f_{i\mu\sigma'}^\dagger f_{i\nu\sigma'} f_{i\nu\sigma}. \end{aligned}$$

Here i and μ are site and orbital indices, respectively. We use a primitive unit cell containing one Fe site with the Brillouin zone indicated in Fig. 2. Wave vectors in this unfolded zone are denoted by dimensionless vectors $\mathbf{k} = \mathbf{Q}a/\sqrt{2}$. We index $\mathbf{k} = k_x \hat{\mathbf{x}} + k_y \hat{\mathbf{y}}$ in a coordinate system rotated by 45° compared to that used for $\mathbf{Q} = H\mathbf{a}^* + K\mathbf{b}^*$ so that $k_x = (H + K)\pi$ and $k_y = (H - K)\pi$.

The bare static susceptibility is

$$\chi_{\mu\rho,\nu\lambda}^0(\mathbf{q}) = \int \frac{d\mathbf{k}}{(2\pi)^2} \sum_{\omega_n} G_{\mu\nu}(\mathbf{k} + \mathbf{q}, \omega_n) G_{\lambda\rho}(\mathbf{k}, -\omega_n)$$

where $\omega_n = (2n + 1)\pi T$ and $G_{\mu\nu}(\mathbf{k}, \omega)$ is the orbital Green's function. The non-zero elements of the $5^2 \times 5^2$ interaction matrix are denoted $\hat{V}_{\mu\mu\mu\mu} = U$, $\hat{V}_{\mu\nu\nu\nu} = U'$, $\hat{V}_{\mu\mu\nu\nu} = J_H$, and $\hat{V}_{\mu\nu\nu\mu} = G_2$, where $\mu \neq \nu$. Within the random phase approximation, the full spin susceptibility is $\chi^s(\mathbf{q}) = \frac{1}{2} \sum_{\mu\nu} \chi_{\mu\mu,\nu\nu}^{RPA}(\mathbf{q})$, where $\chi^{RPA} = \chi^0(1 - V\chi^0)^{-1}$. We simplify the description of the Fe-planes near a magnetic instability by assuming rotational symmetry for interactions, which implies $J_H = G_2$ and $U' = U - J_H - G_2$ [26, 27].

\mathcal{H}_{imp} describes the exchange interaction between the interstitial Fe and neighboring Fe sites:

$$\mathcal{H}_{\text{imp}} = J\mathbf{S} \cdot \sum_{i \in NN} \mathbf{s}_i + J'\mathbf{S} \cdot \sum_{j \in NNN} \mathbf{s}_j. \quad (2)$$

Here $J < 0$ ($J' > 0$) is the FM (AFM) exchange constant between the impurity spin and the four NN (eight NNN) spins in the Fe plane. \mathcal{H}_{imp} is treated as a perturbation to \mathcal{H}_{int} , with the impurity spin fixed. To leading order, we obtain

$$s(\mathbf{k}) = -4\chi^s(\mathbf{k}) \left[J \cos\left(\frac{k_x}{2}\right) \cos\left(\frac{k_y}{2}\right) + J' \left(\cos\left(\frac{k_x}{2}\right) \cos\left(\frac{3k_y}{2}\right) + \cos\left(\frac{3k_x}{2}\right) \cos\left(\frac{k_y}{2}\right) \right) \right] \quad (3)$$

The structure factor, including the contribution of the impurity spin is $\mathcal{S}(\mathbf{Q}) \propto |1 + s(\mathbf{k})|^2$. While χ^s has nesting peaks at $\mathbf{k} = (\pi, 0)$ ($\mathbf{Q} = (\frac{1}{2}, \frac{1}{2})$) [24, 25], these are suppressed by the square bracket in Eq. 3. The fit to the experimental data gives $U = 0.95(5)$ eV, $J_H = G_2 = 0.05(5)$ eV, $J = -70$ meV and $J' = 40$ meV. Consistent with the *effective* nature of \mathcal{H}_{imp} , there is a considerable robustness to the fit: the essential features are the FM J versus AFM J' and $0.2|J| < J' < 0.8|J|$. For comparison, the dominant NN and NNN exchange constants in $\text{Fe}_{1.05}\text{Te}$, with similar Fe-Te-Fe bond angles are $J = -51(3)$ meV and $J' = 22(4)$ meV [28].

The calculated structure factor, $\mathcal{S}(\mathbf{Q})$, is shown in Fig. 2(e)-(f) and corresponding real space magnetization map in Fig. 4(b). Comparing to the experimental data (Fig. 4(a)), there is reasonable agreement up to the third NN beyond which the theory overestimates the magnitude of induced magnetization and modulation along the $(\frac{1}{2}, \frac{1}{2})$ direction. Possible reasons include lack of orbital specificity to the interaction parameters and effects from neighboring interstitial sites. Indeed, the appearance of nominally elastic diffuse magnetic scattering in our experiment indicates a spin-glass like state that links interstitials. Further information about associated spin dynamics was recently provided for $\text{Fe}_{1.01}\text{Te}_{0.72}\text{Se}_{0.28}$ [29].

Confirming indications from resistivity measurements [11] and predictions from Density Functional Theory [30],

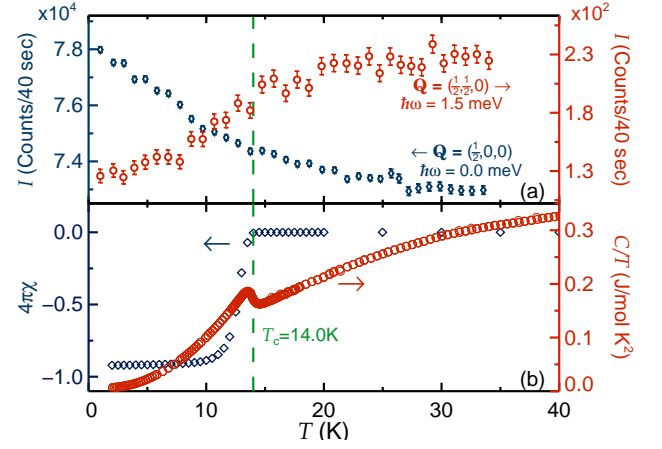


FIG. 5. (a) T -dependence of neutron scattering intensity at $\mathbf{Q}=(\frac{1}{2}, 0, 0)$ and $\hbar\omega = 0.0$ meV (red), and $\mathbf{Q}=(\frac{1}{2}, \frac{1}{2}, 0)$ and $\hbar\omega = 1.5$ meV (blue). (b) DC susceptibility measurement at $\mu_0 H = 3\text{mT}$ (blue diamonds) showing diamagnetic screening which yield an upper bound of 92.9(7)% on the superconducting volume fraction. Specific heat data (red circles) from which a volume fraction of 83% is extracted.

our data show the interstitial site develops a full local moment. Superexchange interactions further enforce FM plaquettes around impurities with fairly large magnetic moments. Sprinkled at random through the sample, these favor spin configurations where the primitive unit cell carries dipole moment so that the $(\frac{1}{2}, 0)$ type double stripe structure emerges as a compromise between the $(\frac{1}{2}, \frac{1}{2})$ semi metallic nesting instability and FM superexchange interactions. Indeed this manifests in our impurity band structure calculation (Fig.2(e)).

We now examine the interplay between interstitial glassy magnetism and superconductivity. Fig. 5(a) shows the T -dependence of inelastic scattering at $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2})$ which is sensitive to magnetic fluctuations linked to s_{\pm} superconductivity [2]. The intensity is precipitously suppressed for $T < T_c$ as the gap opens and the spin resonance develops. The elastic scattering at $(\frac{1}{2}, 0)$ on the other hand grows upon cooling with no apparent anomaly at T_c . Despite the 1% level interstitial concentration, the spatial extent of the associated Friedel oscillation (> 50 neighboring Fe Sites, Fig. 4) ensures the majority of the Fe atoms are involved and thus microscopic coexistence with the $> 80\%$ superconducting volume fraction. The large energy scales ($-J, J' \gg k_B T_c$) that control the interstitial polaron and the different characteristic wave vectors associated with magnetism and superconductivity are surely relevant here. At the same time previous studies show interstitial iron does reduce the superconducting volume fraction [11]. These facts suggest two length scales are involved as in the mixed phase of a type II superconductor: polaron cores accounting for the $\sim 17\%$ normal volume fraction, with Friedel oscillations permeating the superconducting bulk.

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