Coexistence of incommensurate magnetism and superconductivity in Fe$_{1+y}$Se$_x$Te$_{1-x}$

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We report an investigation into the superconducting and magnetic properties of Fe$_{1+y}$Se$_x$Te$_{1-x}$ single crystals by magnetic susceptibility, muon spin rotation, and neutron diffraction. We find three regimes of behavior in the phase diagram for $0 \leq x \leq 0.5$: (i) commensurate magnetic order for $x \lesssim 0.1$, (ii) bulk superconductivity for $x \approx 0.5$, and (iii) a range $0.25 \lesssim x \lesssim 0.45$ in which superconductivity coexists with static incommensurate magnetic order. The results are qualitatively consistent with a two-band mean-field model in which itinerant magnetism and extended s-wave superconductivity are competing order parameters.

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The recently discovered Fe-based high-temperature superconductors (HTS) host an intriguing competition between magnetic, structural and superconducting phases. The parent phases, such as LnOFeAs (Ln1111, Ln=La, Ce, Pr, Sm) and AFexAs$_2$ (A122, A=Ba, Sr, Ca) exhibit commensurate, static, magnetic order. Upon doping or application of pressure (chemical or mechanical), magnetism is suppressed and superconductivity emerges in a manner somewhat dependent on the material. Experiments on fluoridedoped La1111 and Pr1111 indicate that the transition from the superconducting to the magnetic state is of the first-order. Ce1111 shows a behavior which is more consistent with a quantum-critical point separating magnetic and superconducting states. The experiments on Sm1111 and A122 demonstrate co-existence of magnetism and superconductivity.

Recently, Sales et al. reported on the synthesis of large single crystals of Fe$_{1+y}$Se$_x$Te$_{1-x}$ ($0 \leq x \leq 0.5$) belonging to the 011 family of Fe-based HTS. Resistivity measurements showed traces of superconductivity at $T \lesssim 14$ K for all $x \neq 0$ crystals, while bulk superconductivity was detected only for compositions close to $x = 0.5$. Non-superconducting Fe$_{1+y}$Te with $y \lesssim 0.1$ exhibits long-range commensurate magnetic order, but only short-range incommensurate magnetism survives in Se-doped samples. Up to now, however, the relation between the magnetic and superconducting properties has not been studied systematically for this new system. Here we report on a detailed study of the evolution of superconducting and magnetic properties of Fe$_{1+y}$Se$_x$Te$_{1-x}$ single crystals through a combination of magnetic susceptibility, muon spin rotation, and neutron diffraction. At the boundary between magnetic and superconducting phases we observe a region of doping in which superconductivity coexists with incommensurate magnetic order. The phase diagram is qualitatively consistent with a two-band itinerant models of the Fe pnictides in which magnetism and extended s-wave superconductivity are competing orders.

Muon-spin rotation ($\mu$SR) and neutron diffraction (powder and single crystal) experiments were performed on the $\pi$M3 and $\pi$E1 beam lines at Sp$\mu$, and on the HRPT and TASP instruments at SINQ (all at the Paul Scherrer Institute, Switzerland). AC susceptibility measurements were performed on a Quantum Design PPMS magnetometer with a measuring field $\mu_0H_{AC} = 0.1$ mT and frequency $\nu = 1000$ Hz. To reduce the effects of demagnetization thin plate-like pieces of Fe$_{1+y}$Se$_x$Te$_{1-x}$, cleaved from the main single crystals, were oriented with the flat surface ($ab$ plane) parallel to the AC field.

Single crystals of Fe$_{1+y}$Se$_x$Te$_{1-x}$ were grown by a modified Bridgeman method similar to that reported in Ref. [13]. Powders of Fe, Se and Te of minimum purity 99.99% were mixed in the appropriate ratios, pressed into a rod and vacuum sealed in a double-walled quartz ampule. The rod was first melted and homogenized at 1200°C for 4 hours and then cooled in a temperature gradient 8°C/cm at a rate 4°C/h down to 750°C followed by 50°C/h cooling. Several of the crystals were ground into a powder and their phase purity was checked by neutron powder diffraction. The amount of the main (P4/nnm) fraction was found to be $\approx 94\%$, 97%, 98%, and 99% for $x = 0.5$, 0.45, 0.4, and 0.25 crystals, respectively.

The AC susceptibility ($\chi_{AC}$) data are shown in Fig. 1. The $x = 0.5$ and $x = 0.45$ samples are seen to be bulk superconductors with $\chi_{AC} = -1.09$ and $-1.18$, respectively, at $T \approx 2$ K. Values of $|\chi_{AC}|$ in excess of unity are likely explained by small non-zero demagnetization factors caused by slight misalignment of the crystals relative to the direction of the AC field. The $x = 0.4$ and 0.25 samples exhibit superconductivity but have a small superconducting fraction of order 10% at low temperature. No traces of superconductivity were detected for...
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The slightly stronger relaxation is due to randomly-oriented local magnetic fields, which are static internal field. The experiment in ZF provides information on the internal magnetic field distribution, while complementary LF measurements make it possible to discriminate between static and fluctuating fields.

Figure 2 represents μSR results for representative compositions of Fe$_{1+y}$Se$_x$Te$_{1-x}$. Figure 2(a) shows that for $x = 0.5$ there is no difference between the ZF time-spectra measured at $T = 1.7$ K and 20 K. This suggests that the magnetic state of FeSe$_{0.5}$Te$_{0.5}$ is the same above and below the superconducting transition temperature. The solid lines correspond to a fit by the function $A_{ZF}^t = A_{ZE}^t e^{-\Delta_{ZF}^t}$, where $A_{ZE}^t$ is the initial asymmetry and $\Delta_{ZF}^t$ is the exponential relaxation rate. Measurements in LF geometry (not shown) indicate that the exponential character of the muon-spin relaxation is due to randomly-oriented local magnetic fields, which are static on the μSR time scale. Such behavior is consistent with dilute Fe moments as observed recently for another representative of Fe-based HTS FeSe$_{1-y}$Te$_y$ The TF data for $x = 0.5$ fit well to the function $A_{TF}^t (t) = A_{TF}^0 e^{-\lambda_{TF}^t t + \sigma^2/2 t^2} \cos(\gamma_{\mu} B T t + \phi)$. Here, $\gamma_{\mu}/2\pi = 135.5$ MHz/T is the muon gyromagnetic ratio, $\phi$ is the initial phase of the muon-spin ensemble, and $\sigma$ is the Gaussian relaxation rate. The right panel of Fig. 2(a) shows that the TF asymmetry $A_{TF}^0$ is almost temperature independent. The slightly stronger relaxation of the muon-spin polarization at 1.7 K relative to 20 K is due to formation of the vortex lattice at $T < T_c$.

For the $x = 0.45$ sample, Fig. 2(b), there is little change in either the ZF or the TF time spectra on cooling from 20 K to ~7 K. At lower temperatures, however, an additional fast relaxing component starts to develop. The solid lines in Fig. 2(b) (left panel) correspond to fits with $A_{ZF}^t (t) = A_{1ZF}^0 e^{-\Delta_{1ZF}^t t} + A_{2ZF}^0 e^{-\Delta_{2ZF}^t t}$ and $A_{TF}^t (t) = e^{-\sigma^2 t^2/2} [A_{1TF}^0 e^{-\lambda_{1TF}^t t} \cos(\gamma_{\mu} B t + \phi) + A_{2TF}^0 e^{-\lambda_{2TF}^t t} \cos(\gamma_{\mu} B t + \phi)],$ Here, $A_{1ZF(TF)}^0$ and $\Delta_{1ZF(TF)}^t$ are the initial ZF(TF) asymmetry and the exponential depolarization rate of the slow (fast) relaxing component, respectively. The decrease of $A_{TF}^t$ with decreasing temperature (Fig. 2(b) right panel) is due to the development of magnetic order, which at $T \approx 1.7$ K occupies more than 50% of the whole sample volume. The LF measurements reveal that the slow relaxing component completely recovers at $\sim 10$ mT (similar to that observed for the $x = 0.5$ sample), while the asymmetry of the fast relaxing one decreases by ~50% at $B_{LF} = 0.4$ T. Considering that the muon spins become decoupled from the static internal field $B_{int}$ at $B_{LF}^0 \geq 10 B_{int}$, we may...
assume that the magnetism which develops in the $x = 0.45$ sample below $T \sim 7$ K is caused by the static internal field $B_{\text{int}} \gtrsim 0.1$ T at the muon stopping site.

Magnetism was found to develop in the $x = 0.4, 0.25, 0.1,$ and 0.0 samples below $T \simeq 18, 30, 40$ and 70 K, respectively, as signalled by a fast drop of both $A^\text{ZF}$ and $A^\text{TF}$ within the first 100 ns [see Figs. 2(c) and (d); the ZF and TF time spectra for $x = 0.4$ and $x = 0.1$ look very similar to that of the $x = 0.25$ sample and are not shown]. The TF and ZF data for $x = 0.4, 0.25$ and 0.1 were fitted similarly to $x = 0.45$. In order to fit the highly damped oscillations observed for $x = 0$ [Fig. 2(d)] the second term in $A^\text{ZF}(t)$ was multiplied by $\cos(\gamma_B B_{\text{int}} t)$. This sample shows an abrupt change in $B_{\text{int}} \simeq 0.21$ T at $T \simeq 70.6$ K and hysteresis in $A^\text{TF}(T)$ measured on increasing and decreasing temperature — see inset in the right panel of Fig. 2(d). These features are evidence for a first-order magnetic transition in Fe$_{1.03}$Te, consistent with the results of Refs. 20 and 21. To within our experimental accuracy there is no hysteresis in the magnetic transition for the $x = 0.45, 0.4, 0.25$, and 0.1 samples.

The fact that the ZF time spectra for the $x = 0$ sample can be well described by a damped cosine function with zero initial phase [see Fig. 2(d)] suggests that the magnetism in Fe$_{1.03}$Te is commensurate. The absence of ZF oscillations for samples with $x > 0$ prevents any firm conclusions being drawn about the type of magnetism in these samples. To learn how the magnetic correlations change with Se doping we performed neutron diffraction measurements on the $x = 0.25$ crystal. The neutron polarization analysis device MuPAD was employed to separate magnetic from non-magnetic scattering. The inset in Fig. 3 is a color map of the spin-flip (SF) scattering in the $(h,0,l)$ plane in reciprocal space (referred to the tetragonal unit cell with $a \simeq 3.8$ Å and $c \simeq 6.2$ Å). The sample temperature was 2 K, and the neutron wavelength was 3.2 Å. The neutron polarization $\mathbf{P}$ was maintained parallel to the scattering vector $\mathbf{Q}$ so that the SF scattering is purely magnetic. The map reveals a magnetic peak centered on the incommensurate wavevector (0.46, 0.0, 0.5). The peak is broader than the instrumental resolution, and correlation lengths extracted from cuts through the peak parallel to the $a$ and $c$ axes are $\xi_a = 11.5 \pm 1.0$ Å and $\xi_c = 6.0 \pm 0.5$ Å. Figure 3 shows the temperature dependence of the peak intensity at (0.46, 0.0, 0.5) measured with unpolarized neutrons. The magnetic peak emerges below $T \approx 40$ K, consistent with the muon asymmetry data, Fig. 4(c). A recent study on a crystal of Fe$_{1.07}$Se$_{0.25}$Te$_{0.75}$ has also reported incommensurate magnetic order. The incommensurability and $\xi_c$ are consistent with our results, but $\xi_a$ is a factor of 2 smaller than in our sample.

Figure 4 summarizes our results on the magnetism and superconductivity in Fe$_{1+y}$Se$_2$Te$_{1-x}$. The volume fraction curves for the superconducting (SC) and magnetic (M) phases are taken from $\chi_\text{AC}(T)$ (Fig. 1) and $A_1^\text{TF}(T)$ (Fig. 2), respectively. The latter represents the fraction of muons experiencing a static local field. Figure 4(g) shows the mid-point and onset of the superconducting and magnetic transitions, determined as shown in Figs. 1 and 2 as a function of Se content $x$. It can be seen that superconductivity occurs throughout the bulk of the $x = 0.45$ and 0.5 crystals, while it occupies up to $\sim 10\%$ of the sample volume in the $x = 0.25$ and $x = 0.4$ samples as $T \rightarrow 0$. Magnetic order is present in the $x = 0.45, 0.4, 0.25, 0.1,$ and 0.0 samples with respective volume fractions $\geq 75\%, 98\%, 98\%, 95\%,$ and 92$\%$ at $T \rightarrow 0$.

Most interestingly, superconductivity and magnetism are shown to coexist within certain temperature ranges in the $x = 0.45, 0.4$ and 0.25 samples. For $x = 0.45$, magnetism starts to develop below the superconducting transition temperature [Fig. 4(b)], while in $x = 0.4$ and 0.25 magnetism appears first and superconductivity emerges at a lower temperature [Figs. 4(c) and (d)]. The data do not show any evidence that one form of order emerges at the expense of the other, for if that were the case then a growth in one order parameter would coincide with a decrease in the other. This is clearly not the case, as may be seen in Figs. 4(b)–(d). Nor do the data provide any evidence for macroscopic phase separation into superconducting and magnetic clusters (bigger than a few nm in size), as observed e.g. for Ba$_{1-x}$K$_x$Fe$_2$As$_2$. In such a case the sum of magnetic and superconducting volume fractions at a given $T$ should never exceed unity as they do here, especially for $x = 0.45$.

To account for the coexistence of superconductivity and magnetism in Fe$_{1+y}$Se$_2$Te$_{1-x}$ we consider two scenarios. The first possibility is a nanoscale segregation into magnetic domains, similar to that reported for cuprate HTS. In underdoped cuprate HTS, static, short-range, stripe-like magnetic correlations are thought to exist in the superconducting state and are assumed not to affect the superconducting carriers. Muons are sensitive to dipolar fields at a distance of up to a few lattice spacings, so if nano-scale magnetic domains exist then the fraction of muons experiencing static local magnetic fields could be significantly higher than the fraction of Fe.
FIG. 4: (Color online) (a)–(f) Temperature dependence of the superconducting (SC) and magnetic (M) volume fractions in Fe$_{1.03}$Se$_y$Te$_{1−x}$. PM denotes the paramagnetic phase. (g) Phase diagram showing $T_{c}^{\text{onset}}$, $T_{c}^{\text{mid}}$, $T_{c}^{\text{met}}$, and $T_{c}^{\text{mid}}$ as a function of $x$. The datum for FeSe$_{1−x}$ is from Ref. 24.

sites carrying an ordered moment. On the other hand, no evidence has been found yet for local magnetic domains in Fe-based compounds. In fact, a recent nuclear magnetic resonance study of Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ showed the appearance of magnetic order on all Fe sites thus ruling out nano-scale segregation in that material.

The second possibility is a coexistence of the two order parameters on the atomic scale. The combination of incommensurate magnetism and superconductivity is compatible with models recently proposed in Refs. 24, 25. According to Ref. 24 when $T_{c}^{\text{onset}}/T_{c}^{\text{max}} ∼ 1$, where $T_{c}^{\text{onset}}$ is the magnetic ordering temperature at zero doping ($x = 0$) and $T_{c}^{\text{max}}$ is the maximum value of the of the superconducting transition temperature for a given family of Fe-based HTS, the magnetic order is commensurate and the transition between the magnetic and superconducting phases with $x$ is first order. However, for larger $T_{c}^{\text{onset}}/T_{c}^{\text{max}}$ the transition between commensurate magnetic order and superconductivity goes through a region of $x$ where superconductivity coexists with incommensurate magnetic order. In the series Fe$_{1+y}$Se$_x$Te$_{1−x}$ studied here we find just such behavior. It is a commensurate magnet without superconductivity at $x = 0$, and a nonmagnetic superconductor at $x = 0.5$. In between, at $x = 0.25$, we observe incommensurate magnetism coexistent with $\sim 10%$ superconducting fraction. These results are encouraging for the model, but details still need to be worked out. For example, both LaFeAsO$_x$F$_{1−x}$ and Fe$_{1+y}$Se$_x$Te$_{1−x}$ have $T_{c}^{\text{onset}}/T_{c}^{\text{max}} ∼ 5$, yet LaFeAsO$_x$F$_{1−x}$ apparently exhibits a first-order transition between magnetic and superconducting phases as a function of $x$ without an intermediate region of coexistence.

In conclusion, the phase diagram of Fe$_{1+y}$Se$_x$Te$_{1−x}$ bears a strong resemblance to that of other iron pnictide superconductors, but the existence of an intermediate range of doping in which superconductivity coexists with incommensurate magnetic order appears to be specific to Fe$_{1+y}$Se$_x$Te$_{1−x}$. The existence of such a phase has been predicted theoretically and is of particular interest in view of the possibility of a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state.

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