Strong \((\pi, 0)\) spin fluctuations in \(\beta\)-FeSe observed by neutron spectroscopy

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We have performed powder inelastic neutron scattering measurements on the unconventional superconductor \(\beta\)-FeSe (\(T_c \approx 8\) K). The spectra reveal highly dispersive paramagnetic fluctuations emerging from the square-lattice wave vector \((\pi, 0)\) extending beyond 80 meV in energy. Measurements as a function of temperature at an energy of \(\sim 13\) meV did not show any variation from \(T_c\) to 104 K. The results show that FeSe is close to an instability towards \((\pi, 0)\) antiferromagnetism characteristic of the parent phases of the high-\(T_c\) iron arsenide superconductors, and that the iron magnetic moment is neither affected by the orthorhombic-to-tetragonal structural transition at \(T_s \approx 90\) K nor does it undergo a change in spin state over the temperature range studied.

Iron selenide (\(\beta\)-Fe\(_{1+x}\)Se, hereafter denoted “FeSe”) is structurally the simplest of the iron-based superconductors but it is also one of the most intriguing. The superconducting transition temperature of the pure bulk phase is relatively low, \(T_c \approx 8\) K \(^1\), but it increases to 37 K under pressure \(^2\) and rises above 40 K with intercalation of alkali ions \(A^+\) to form \(A_x\)Fe\(_{2-y}\)Se\(_2\) \(^3\) or by co-intercalation of ammonia molecules and amide ions or organic molecules along with \(A^+\) \(^4\)-\(^6\). Very recently, evidence has been presented for superconductivity at temperatures as high as 100 K in monolayers of FeSe on SrTiO\(_3\) \(^7\)-\(^8\). Although there is evidence that superconductivity at ambient pressure is favored by reduction of Fe below the +2 oxidation state and minimisation of vacancies in the FeSe layers \(^9\)-\(^9\), there is currently no simple explanation for such an extraordinary variation in \(T_c\) among derivatives containing very similar antifluorite layers of FeSe.

The structural and electronic ordering properties of FeSe differ qualitatively from those of the related iron pnictide compounds in two important ways. First, superconductivity appears in FeSe without the need for doping and is very sensitive to composition \(^10\). Second, FeSe has a tetragonal-to-orthorhombic structural transition (\(T_s \approx 90\) K \(^11\)), as in the parent phases of the iron pnictide superconductors, but this transition is not followed by the development of long-range magnetic order \(^12\). The phase below \(T_s\) is considered to be some form of electronic nematic, but opinions divide over whether the nematic transition is driven by orbital ordering \(^13\)-\(^16\) or by spin degrees of freedom \(^17\)-\(^20\).

This paper reports measurements of collective paramagnetic spin fluctuations in FeSe. Spin fluctuations are a prominent feature of the iron-based superconductors and are thought to play a significant role in the pairing interaction \(^21\)-\(^23\). In the iron arsenide superconductors, spin fluctuations emerge from the same (or nearly so) characteristic in-plane wave vector \(q_{m} = (\pi, 0)\), referred to the Fe square sub-lattice, as the spin density wave (SDW) order of the parent phases. This magnetic instability is understood to be assisted by nesting of hole and electron Fermi surface pockets centred around the \(\Gamma\) and \(X\) points of the square lattice. Spin fluctuations have also been observed in the superconducting iron selenides, but the characteristic wave vector varies from system to system. For example, it is \((\pi, 0)\) in \(FeTe_{1-x}Se_x\) \((x \approx 0.5)\) \(^24\), \((\pi, \pi/2)\) in \(A_xFe_{2-y}Se_2\) \((A = K, Rb, Cs)\) \(^25\)-\(^27\), and different again in \(Li_x(ND_2)_y(ND_3)_{1-y}Fe_2Se_2\) \(^28\).

\(Ab\ initio\) electronic structure calculations indicate that FeSe is close to a magnetic ordering instability with characteristic wave vector \((\pi, 0)\) \(^28\)-\(^31\). However, angle-resolved photoemission spectroscopy and quantum oscillation studies have revealed that the Fermi surface deviates significantly from the predictions \(^31\)-\(^32\),\(^34\), and several models for the nematic phase predict competing magnetic phases with \(q_{m} = (\pi, \xi)\), \(0 \leq \xi \leq \pi/2\) \(^17\)-\(^20\).

Experimental information on the magnetic ground state of FeSe is currently lacking, and is urgently needed to elucidate the nematic phase and to assess the role of spin fluctuations in the superconducting state.

Here we report observations of the wave vector and energy dependence of the spin fluctuations in FeSe by powder inelastic neutron scattering. We find collective spin fluctuations emerging from \((\pi, 0)\) and equivalent square-lattice wave vectors, extending to energies greater than 80 meV. We do not observe any significant change in the low energy \((\sim 10-15\) meV) part of the spectrum on crossing the orthorhombic-to-tetragonal transition.

A powder sample of FeSe of total mass 13.8 g was prepared in five separate batches of 2-3 g each. All handling was carried out in an argon atmosphere. Iron and selenium powders (5N purity) were ground together, sealed under vacuum in a silica glass ampoule and reacted at 700°C for 24 h. The product of this reaction was reground, reheated under vacuum, annealed at 700°C for 38 h and then cooled to 400°C and held for 6 days. The ampoule was then quenched in ice water and the sample ground to a fine powder. The batches were found to be
FIG. 1. (color online). (a) Magnetic susceptibility of FeSe powder. The field-cooled (FC) and zero-field cooled (ZFC) curves confirm the onset of superconductivity at \( T_s \approx 8 \text{ K} \) (left). The tetragonal-to-orthorhombic structural transition at \( T_s \approx 90 \text{ K} \) is signalled by a broad magnetic anomaly (right). (b) Rietveld refinement against room temperature neutron powder diffraction data of FeSe. Peak positions for the \( \beta \)-FeSe phase are marked by vertical red ticks beneath the data. The other ticks indicate peak positions for Fe impurities and the vanadium sample can. (c) Temperature dependence of the orthorhombic lattice parameters of FeSe. The points at 150 K are the tetragonal parameters with \( a \) multiplied by \( \sqrt{2} \). The lines are visual guides.

The spectra were normalised to the incoherent scattering from a standard vanadium sample measured with the same incident energies, enabling us to present the data in absolute units of \( \text{mb sr}^{-1} \text{meV}^{-1} \text{f.u.}^{-1} \) (where f.u. refers to one formula unit of FeSe).

Figure 2(a) shows an intensity map of part of the \( E_i = 100 \text{ meV} \) spectrum measured at 8 K on MERLIN. The spectrum is dominated by scattering from phonons when the energy \( E \) is below the phonon cut-off at 40 meV [37]. Above 40 meV, there is a broad vertical column of scattering centred on the wave vector \( Q = 2.6 \text{ Å}^{-1} \), and a weaker column centred on 3.5 \( \text{Å}^{-1} \). Figure 2(b) is a similar intensity map measured with \( E_i = 34 \text{ meV} \) to probe the low \((Q,E)\) part of the spectrum. Phonon scattering dominates in this regime, but there is a window between 10 and 15 meV in which the phonon signal is small, and a vertical column of weak scattering can be seen centred near \( Q = 1.2 \text{ Å}^{-1} \). Such scattering columns are observed in neutron powder spectra of other iron-based superconductors and have been confirmed to arise from strongly dispersive spin fluctuations [38-41].

The magnetic signals identified in the intensity maps can be seen in more detail in \( Q \) cuts taken through the spectrum at fixed average energy, shown in Fig. 3. The cuts contain peaks centered on \( Q = 1.2, 2.6 \) and 3.5 \( \text{Å}^{-1} \), and there are additional weak signals near \( Q = 4.5 \text{ Å}^{-1} \). The series of magnetic peaks can be indexed as orders of the square lattice wave vector \((\pi, 0)\), see Fig. 3(a). In reality, the magnetic signal will extend in the out-of-plane direction, either as a diffuse rod of scattering if the correlations are quasi-two-dimensional or as a series of peaks if there are strong inter-layer correlations. Simulations of such types of out-of-plane scattering show that after powder averaging the peaks have a tail on the high \( Q \) side but the maxima shift by only a small amount \((< 0.06 \text{ Å}^{-1})\) from the ideal two-dimensional wave vectors.
Although FeSe does not order magnetically, our results show that it has a strong magnetic response at \((\pi, 0)\) and equivalent positions which characterise the in-plane SDW order found in the parent phases of the iron arsenide superconductors. To quantify the analysis, we compare the data to a phenomenological model for the low energy response of a two-dimensional (2D) antiferromagnetically-correlated paramagnet. The model has been used previously to describe the low energy part of the spectrum of superconducting Ba(Fe\(1-x\)Co\(x\))\(_2\)As\(_2\) \([12]\). The neutron scattering cross section may be written

\[
\frac{d^2\sigma}{d\Omega dE_i} = \frac{k_i}{k_1} S(Q, E),
\]

where \(S(Q, E)\), the magnetic response function, is the quantity presented here. For an isotropic paramagnet,

\[
S(Q, E) = \left(\frac{\gamma r_0}{2\mu_B}\right)^2 \frac{1}{1 - \exp(-\beta E)} \frac{2}{\pi} f(Q) \chi''(Q, E),
\]

where \((\gamma r_0/2)^2 = 72.7\) mb, \(\beta = 1/k_0 T\), \(f(Q)\) is the magnetic form factor, and \(\chi''(Q, E)\) is the absorptive part of the generalized susceptibility. The low-energy magnetic excitations are envisaged as damped spin waves with a linear dispersion, and we use a harmonic oscillator model

\[
\chi''(q, E) \propto \frac{2E_q^2 E}{(E_q^2 - E^2)^2 + 4\Gamma^2 E^2},
\]

in which \(E_q = \hbar (v_x q_x)^2 + (v_y q_y)^2\) is an anisotropic dispersion with velocities \(v_x\) and \(v_y\) in the longitudinal and transverse directions relative to \(q_m = (\pi, 0)\). \(\Gamma = \gamma E\) is the inverse lifetime, and \(q\) is the spin-wave wave vector. \(\chi''(q, E)\) does not vary with \(q_z\), and is repeated in 2D momentum space with the periodicity of the 2D magnetic wave vector \(q_m\). We fixed \(\gamma = 0.15\), as in Ref. \([12]\), and adjusted \(v_x, v_y\), an intensity scale factor and a linear background to achieve a good fit to the constant-energy cuts. An extra \(Q^4\) term was added to data above the phonon cut-off to model the small multiphonon background. The experimental \(Q\) resolution was included.

The best agreement was found with \(v_x = 500\) meV\(\AA\) and \(v_y = 150\) meV\(\AA\), and is shown in Figs. 2(b). The simulations match the peak near \(Q = 1.2\) \(\AA^{-1}\) and closely
reproduce the observed dispersion of the signals centered near \( Q = 2.6, 3.5 \) and 4.5 Å\(^{-1}\). The model parameters are similar to those found for Ba(Fe\(_{1-x}\)Co\(_x\))\(_2\)As\(_2\): \( v_x = 580 \text{ meVÅ}, \ v_y = 230 \text{ meVÅ} \) [12]. We also attempted to model the data with an isotropic spin-wave velocity but could not obtain an acceptable fit for all \( Q \). Therefore, the analysis strongly favours an anisotropic velocity.

Despite the limitations inherent in powder-averaging, the success of the model in accounting for the features in the data over several Brillouin zones places a tight constraint on the wave vector \( \mathbf{q}_m \) that describes the dominant mode of paramagnon excitations in FeSe. To demonstrate this, Fig. 3(c) shows the result of the calculation when a wave vector \( \mathbf{q}_m = (\pi, \pi/4) \) is assumed instead of \((\pi, 0)\). The double-peak signal near 2.6 Å\(^{-1}\) is seen to shift to significantly lower \( Q \), reflecting the difference between the magnitude of the wave vector \((\pi, 2\pi)\), \( Q = 2.64 \text{ Å}^{-1}\), and \((\pi, 7\pi/4)\), \( Q = 2.38 \text{ Å}^{-1}\) — see Fig. 3(a). Considering magnetic wave vectors of the general form \( \mathbf{q}_m = (\pi, \xi) \), we obtained acceptable fits only for \( |\xi| \lesssim \pi/10 \).

In this experiment we were unable to cool the sample below 8 K, and so did not study the magnetic signal in the superconducting state at low energies where a spin resonance could be expected. Instead, we investigated the influence of the structural transition on the magnetic response by performing runs with \( E_i = 50 \text{ meV} \) at temperatures of 8, 17, 67 and 104 K. Figure 4 shows \( Q \) cuts through the \((\pi, 0)\) position at each temperature. The data are averaged over the energy interval from 11 to 14 meV to stay within the window where phonon scattering is weak. The magnetic peaks show very little variation with temperature. To quantify this, we fitted a Gaussian function on a linear background to each cut. To within the fitting error the integrated intensity remains constant at \( 0.10 \pm 0.01 \text{ mb sr}^{-1} \text{ meV}^{-1} \text{ Å}^{-1} \text{ f.u.}^{-1} \), which is similar to the spectral weight found in the same energy range for LiFeAs at \( T = 20 \text{ K} > T_c \) [11].

The fact that the magnetic response shows very little or no change on crossing the structural phase transition implies that the structural transition is not driven by magnetic fluctuations at the frequencies probed in our experiment. Further, the lack of any change over the entire temperature range studied implies that the paramagnetic moment is constant below 104 K, in contrast with the notion of a gradual spin-state transition proposed to explain thermally-induced phonon anomalies observed in Raman spectra [43].

This study establishes that the collective spin fluctuations in FeSe share many similarities with those in the high-\( T_c \) Fe arsenide superconductors, including a very steep dispersion and a low frequency response that is strongest at or very close to the square lattice wave vector \((\pi, 0)\). We find no direct evidence for competing magnetic orders, although the highly anisotropic spin-wave velocity implies a greater tendency for transverse spin fluctuations. If spin fluctuations are important for the pairing mechanism in Fe-based superconductors then our results show that the ingredients for high-\( T_c \) are present in FeSe, and something other than conventional magnetic dipole fluctuations must compete with superconductivity. Several different nematic degrees of freedom that could suppress superconductivity have been discussed recently [13, 20], and experiments to search for possible orbital and spin nematic order parameters compatible with \((\pi, 0)\) spin fluctuations will be an important next step.

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