



Suppression of antiferromagnetic spin fluctuations in the collapsed phase of CaFe_2As_2

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Inelastic neutron-scattering measurements of CaFe_2As_2 under applied hydrostatic pressure show that the antiferromagnetic spin fluctuations observed in the ambient pressure, paramagnetic, and tetragonal (T) phase are strongly suppressed, if not absent, in the collapsed tetragonal (cT) phase. These results are consistent with a quenched Fe moment in the cT phase and the strong decrease in resistivity observed upon crossing the boundary from the T to cT phases. The suppression or absence of static antiferromagnetic order and dynamic spin fluctuations in the nonsuperconducting cT phase supports the notion of a coupling between spin fluctuations and superconductivity in the iron arsenides.

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Although there is, as yet, no consensus regarding the pairing mechanism that gives rise to superconductivity in the iron arsenides, a great deal of activity has focused on the role of spin fluctuations and the proximity of superconductivity to structural and magnetic instabilities. In particular, recent inelastic neutron-scattering measurements on polycrystalline $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ (Ref. 1) as well as single crystals of $\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2$ (Ref. 2) and $\text{Ba}(\text{Fe}_{0.95}\text{Ni}_{0.05})_2\text{As}_2$ (Ref. 3) have found evidence of a resonant spin excitation at energies above a gap that opens in the superconducting state. These resonances are found at energies corresponding to approximately $5k_B T_c$, similar to those observed for the high T_c cuprates.⁴ Furthermore, single-crystal measurements^{2,3} have shown that this resonance is found at the same wave vector, $(\frac{1}{2}\frac{1}{2}L)$ for L odd, as the static magnetic order in the undoped $A\text{EFe}_2\text{As}_2$ ($A\text{E}=\text{Ca}, \text{Sr}, \text{Ba}$) parent compounds,^{5–8} again highly reminiscent of the cuprates. The interplay between spin dynamics and superconductivity has also been reported for intermetallic compounds such as UPd_2Al_3 ,⁹ CeCoIn_5 ,¹⁰ and CeCu_2Si_2 .¹¹ All of these results suggest that spin fluctuations are coupled to charge carriers and may play an important role for superconductivity in the iron arsenide compounds.

Superconductivity in the parent $A\text{EFe}_2\text{As}_2$ compounds under applied pressure has been reported by several groups using liquid-media pressure cells.^{12–18} For CaFe_2As_2 , however, recent measurements¹⁹ under hydrostatic pressure conditions (He-pressure cell) have revealed that superconductivity, if present at all, occurs in a very narrow range of pressure close to the reported orthorhombic-to-collapsed tetragonal (O - cT) phase transition (see Fig. 1).^{20,21} This work concluded that a nonhydrostatic pressure component may cause the formation of domains and domain walls with varying properties, including superconductivity.¹⁹ Therefore, while the conditions necessary for superconductivity in BaFe_2As_2 and SrFe_2As_2 remain an open question, it appears that, under hydrostatic conditions, the cT phase in CaFe_2As_2 does not support superconductivity. There is also evidence that the cT

phase in CaFe_2As_2 , in contrast to the tetragonal (T) and orthorhombic (O) phases, is nonmagnetic.^{20,21} Elastic neutron-scattering measurements under hydrostatic pressure (He-pressure cell), for example, have shown that the ordered moment of approximately $0.8\mu_B$ found for the antiferromagnetic O structure below $p=0.35$ GPa disappears abruptly at the O - cT transition.²¹ Furthermore, there is a striking increase in the conductivity of CaFe_2As_2 upon traversing the tetragonal-to-collapsed tetragonal (T - cT) phase boundary^{12,13,19} even though band-structure calculations show that the density of states at the Fermi energy is reduced by nearly 60% in the cT phase.¹⁷ One possible explanation for this discrepancy is the elimination of spin scattering contributions to the resistivity on transforming from the T phase to cT phase.

Here, we report on inelastic neutron scattering from spin fluctuations in CaFe_2As_2 under hydrostatic pressure. Approximately 300 Sn-flux-grown single crystals of CaFe_2As_2 (Ref. 22) with a total mass of 1.5 g were coaligned on both sides of a set of aluminum plates [see Fig. 1(a)] such that their common $[H H 0]$ and $[0 0 L]$ axes (using the tetragonal unit-cell notation) were coincident with the scattering plane. One of the challenges in this measurement lies in the nature of the T - cT transition in CaFe_2As_2 . As described in Refs. 20 and 21, there is a striking change in the unit-cell dimensions upon transformation to the cT phase; the c lattice parameter decreases by 9% while the a lattice parameter increases by 2%. Our experience has shown that because CaFe_2As_2 is quite soft, constrained samples exhibit an extended coexistence between the cT and O or T phases. This coexistence is also observed when nonhydrostatic pressure is applied.²¹ Therefore, only a light coating of fluorine-based (Fomblin) oil was used to maintain contact between the Al plates and the crystals. However, we have also found that this method can lead to changes in the alignment of crystals or the detachment and loss of some crystals at the cT transition. The Al plates holding the samples were stacked and placed in the well of an Al-alloy He-gas pressure cell to

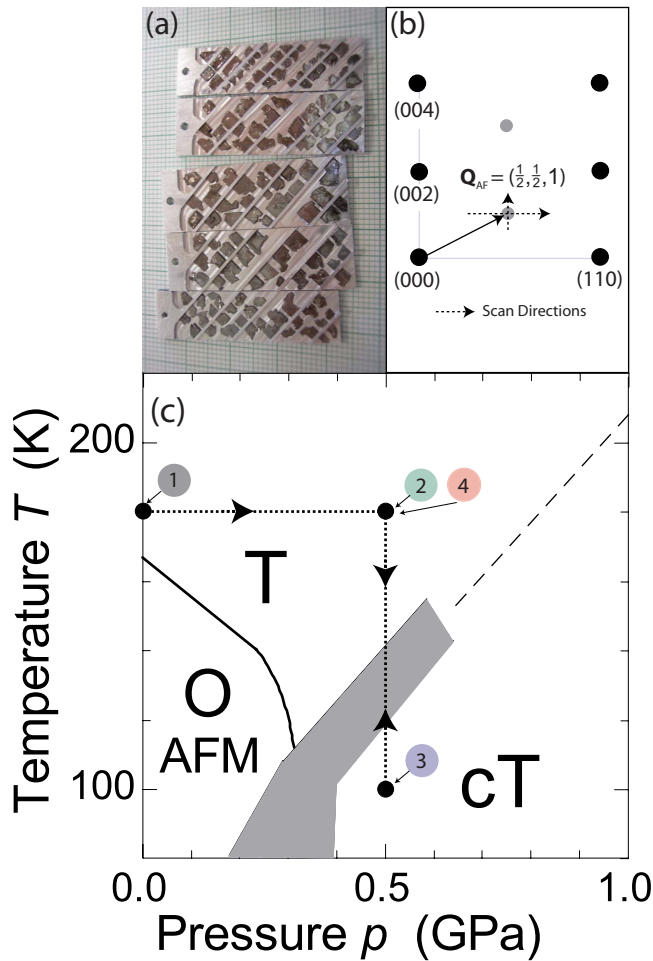


FIG. 1. (Color online) (a) Coaligned single crystals of CaFe_2As_2 . Approximately 300 crystals were mounted on both sides of five Al plates that were stacked to produce the measurement sample (shown on a millimeter grid). (b) Schematic of the reciprocal lattice plane probed in these measurements. The dashed lines denote scans along the $[H H 0]$ and $[0 0 L]$ directions. (c) The p - T phase diagram of CaFe_2As_2 (after Ref. 21). The shaded area represents hysteretic regions, and the numbers correspond to the measurement sequence as described in the text.

ensure hydrostatic pressure conditions. The cell was connected to a pressure intensifier through a high-pressure capillary that allowed continuous monitoring and adjustment of the pressure. Using this system, the pressure could be varied at fixed temperatures for $T > 50$ K (above the He solidification line), or the temperature could be changed at nearly constant pressures.

The inelastic neutron-scattering measurements were performed on the IN8 triple-axis spectrometer at the Institut Laue-Langevin (ILL) at a fixed final energy of 14.7 meV employing a double focusing Si(111) monochromator, a double focusing PG(002) analyzer, and an open collimation. A graphite filter was used after the sample to reduce harmonic contamination of the beam. The energy resolution in this configuration, measured using a vanadium standard, was 1.1 meV full width at half maximum (FWHM). The sample mosaic with respect to both the $[H H 0]$ and $[0 0 L]$ directions was initially 1.6° FWHM at ambient pressure and in-

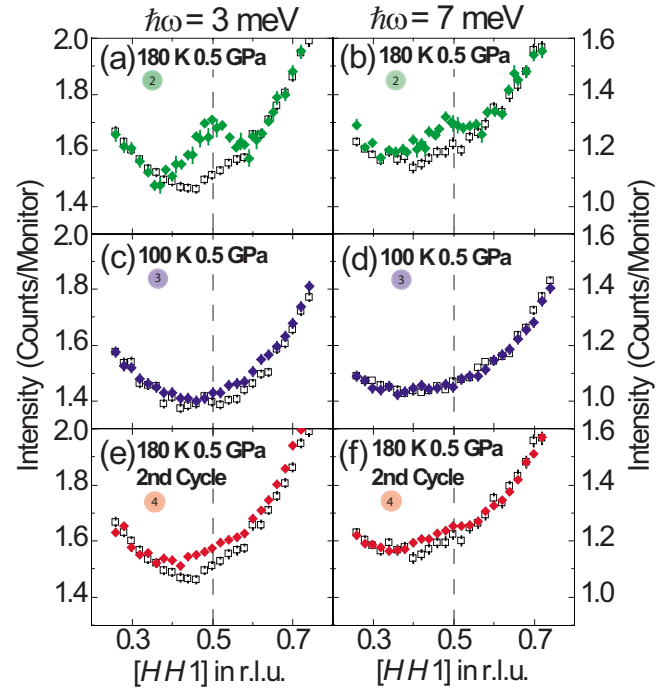


FIG. 2. (Color online) Constant energy \mathbf{q} scans at 3 and 7 meV energy transfer through the $(\frac{1}{2}, \frac{1}{2}, 1)$ antiferromagnetic wave vector along the in-plane $[H H 0]$ direction at $T=180$ K and $p=0.5$ GPa for (a) and (b); $T=100$ K and $p=0.5$ GPa for (c) and (d). Panels (e) and (f) show the data taken at $T=180$ K and $p=0.5$ GPa after passing through the T - cT transition twice (upon cooling and warming). The open squares denote the empty can background measurements. The dashed vertical line denotes the position of the $(\frac{1}{2}, \frac{1}{2}, 1)$. Each data point in this figure represents 6 min of counting time (8000 monitor counts).

creased slightly to 2° at $p=0.5$ GPa. The pressure cell was loaded into an Institut Laue-Langevin Orange-type cryostat allowing temperature control from 300 down to approximately 2 K.

Figures 1(b) and 1(c) describe the regions of reciprocal space and the p - T phase diagram investigated in these measurements. The inelastic scattering was studied primarily around the $(\frac{1}{2}, \frac{1}{2}, 1)$ antiferromagnetic wave vector (using the indices appropriate to the tetragonal unit cell). Constant energy \mathbf{q} scans were measured at several energies along both the $[H H 0]$ and $[0 0 L]$ directions in order to characterize the spin fluctuations at selected temperatures and pressures. The sequence of measurements is depicted in Fig. 1(c). Since we have already established that crossing the phase boundaries into the cT phase from either the O or T phase can significantly increase the mosaic of the sample,¹⁷ care was taken to first measure the inelastic scattering at point 1 (ambient pressure in the tetragonal phase) and point 2 ($p=0.5$ GPa but still in the tetragonal phase) before lowering temperature and crossing over into the cT phase itself (point 3). The scans at $p=0.5$ GPa were repeated using the same pressure cell containing only the aluminum slides coated with the fluorine-based oil and the He-pressure medium to determine the background contribution to the observed scattering. Measurements of the spin-wave dispersion in the O phase at ambient pressure ($T=140$ K) were also done prior

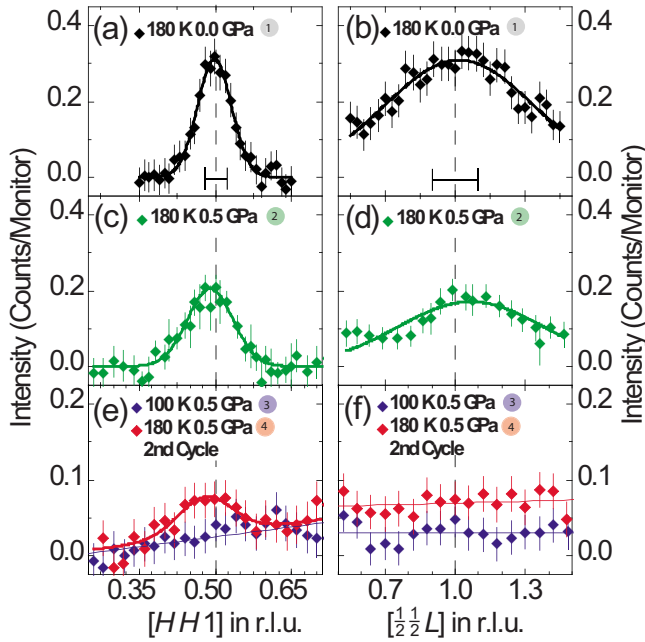


FIG. 3. (Color online) Constant energy \mathbf{q} scans, after background subtraction, at 3 meV energy transfer through the $(\frac{1}{2}\frac{1}{2}1)$ antiferromagnetic wave vector along the $[H H 0]$ [panels (a), (c), and (e)] and the $[0 0 L]$ directions [panels (b), (d), and (f)]. The numbers in the shaded circles correspond to the points indicated in Fig. 1(c). The heavy lines through the data are fits to a single Gaussian line shape. The thin lines provide a guide to the eyes. The dashed vertical line denotes the position of the $(\frac{1}{2}\frac{1}{2}1)$. The instrumental resolution is shown at the bottom of panels (a) and (b).

to pressurizing the system for comparison with previous measurements by McQueeney *et al.*²³ and are consistent with those results. Furthermore, no evidence of static magnetic order at the antiferromagnetic Bragg point in the T or cT phase was observed, consistent with previous results.^{20,21,23}

Figure 2 displays the raw data from constant energy \mathbf{q} scans through the $(\frac{1}{2}\frac{1}{2}1)$ reciprocal lattice position along the $[H H 0]$ direction at $\hbar\omega=3$ and 7 meV energy loss. This is the same wave vector where correlated spin fluctuations have been observed in the Co- and Ni-doped BaFe_2As_2 compounds.^{2,3} The open squares in this figure denote the measured, empty can, background data. Figures 2(a) and 2(b) clearly show the presence of correlated spin fluctuations centered on the antiferromagnetic $(\frac{1}{2}\frac{1}{2}1)$ wave vector for both 3 and 7 meV. As temperature was lowered, at a constant pressure of 0.5 GPa, the sample transformed from the higher temperature T phase to the lower temperature cT phase at approximately 120 K. The absence of a clear signal above the empty can background in Figs. 2(c) and 2(d) indicates that the antiferromagnetic spin fluctuations in the cT phase [point 3 in Fig. 1(c)] are strongly suppressed, if not completely absent. Unfortunately, in the process of transforming from the T to the cT phase, there was an unavoidable increase in the sample mosaic from approximately 2° FWHM at 180 K and 0.5 GPa to nearly 5° FWHM at 100 K and 0.5 GPa. Furthermore, the integrated intensity of the nuclear peaks measured in rocking scans decreased by approximately 40%, indicating that at least a portion of the sample was

either dislodged or tilted well beyond the measured mosaic (verified by visual inspection after the experiment). Therefore, the temperature was increased back to 180 K to investigate the impact of the broadened mosaic and decreased sample scattering volume on our ability to observe the spin fluctuations. Crossing the cT - T phase line again increased the sample mosaic to nearly 6.5° but did not affect the integrated intensities of the nuclear peaks. Figures 2(e) and 2(f) demonstrate that although the magnetic scattering is broadened and decreased relative to the first measurement at 180 K and 0.5 GPa, it remains clearly in evidence, reaffirming that the correlated spin fluctuations in the T phase of CaFe_2As_2 are strongly suppressed or absent in the cT phase.

In Fig. 3 we compare the inelastic-scattering data taken at $(\frac{1}{2}\frac{1}{2}1)$, along both the $[H H 0]$ direction and the $[0 0 L]$ direction, after subtracting the empty can background, at points 2, 3, and 4. We also show the ambient pressure data taken at 180 K (point 1) in Fig. 1(c) where the background was estimated from the wings of the constant energy \mathbf{q} scan along $[H H 0]$. Using a single Gaussian line shape to fit the data in Fig. 3(a) we obtain a dynamic spin-correlation length of $25 \pm 5 \text{ \AA}$ at 3 meV along $[H H 0]$, quite similar to the value obtained from similar measurements on $\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2$.² The corresponding scan along $[0 0 L]$ [Fig. 3(b)] is approximately 50% broader, implying spin correlations perpendicular to the Fe-As planes with a shorter correlation length, again consistent with the findings of Lumsden *et al.*² Upon increasing the pressure to 0.5 GPa at 180 K [Figs. 3(c) and 3(d)], both constant energy \mathbf{q} scans evidence additional broadening, beyond that due to the small increase (0.4°) in the sample mosaic, indicating that the range of antiferromagnetic spin correlations decreases with increasing pressure. Figures 3(e) and 3(f) show the background subtracted constant energy \mathbf{q} scans at 100 K in the cT phase (blue diamonds) and after heating the sample back to 180 K in the T phase (red diamonds). No clear structure is observed in the cT phase data along the $[H H 0]$ direction [Fig. 3(e)], while a reduced and broadened peak at $(\frac{1}{2}\frac{1}{2}1)$ is apparent in the remeasured data at 180 K. The increased width of the peak and reduced intensity is consistent with the increased sample mosaic and loss in sample scattering volume. The corresponding remeasured scan along $[0 0 L]$ at 180 K [Fig. 3(f)] is nearly transverse and, therefore, affected more by the increased sample mosaic. Nevertheless, scattering above the cT phase data can still be seen.

The observation of antiferromagnetically correlated spin fluctuations in the T phase, as well as their strong suppression or complete absence in the cT phase, provides interesting perspectives concerning both the physical properties of CaFe_2As_2 and, more generally, superconductivity in the iron arsenides. Previous elastic neutron-scattering studies^{20,21} have already provided strong evidence for the absence of static magnetic ordering in the cT phase. Total-energy calculations²⁰ have shown that the Fe moment in the cT phase should be quenched. Our results are consistent with the absence of static order and low-energy magnetic fluctuations in the cT phase at $(\frac{1}{2}\frac{1}{2}L)$ for L odd. The possibility that these low-energy spin fluctuations are redistributed to other locations in momentum space cannot be excluded and deserves further exploration through both experiment and theory.

Transport measurements in CaFe_2As_2 under pressure show that there is a significant decrease in the resistivity as the sample transforms from the T phase to the cT phase. Although measurements performed with liquid pressure media^{12,15,16} found a broad change in the resistivity, recent measurements using a He-pressure cell¹⁹ observe sharp, discontinuous changes coincident with the first-order T - cT structural transition determined by elastic neutron-scattering experiments.²¹ The differences in the measured transport properties appear to arise from the influence of a nonhydrostatic component in the liquid-media/clamp cell measurements. The higher conductivity of the cT phase can, in the simplest model, be associated with either an increase in the electronic density of states or a decrease in the scattering (assuming that possible changes in Fermi velocities and phonon spectra are of lesser importance). Band-structure calculations indicate a decrease in the electronic density of states (primarily Fe $3d$ contributions) at the Fermi energy when the sample transforms from the T to cT phase,^{21,24} suggesting that a reduction in electronic scattering plays an important role in the increase in the cT phase conductivity. Here, we have shown that scattering, arising from the presence of antiferromagnetically correlated spin fluctuations, is reduced or eliminated in the cT phase.

The nature of the spin-fluctuation contribution to electronic scattering certainly warrants further investigation, but it seems clear that the antiferromagnetic spin fluctuations in CaFe_2As_2 are coupled to the charge carriers, similar to what

was found for the K-, Co-, and Ni-doped BaFe_2As_2 superconductors. Therefore, it is important to consider these results in the context of prior inelastic-scattering measurements on the doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$,¹ $\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2$,² and $\text{Ba}(\text{Fe}_{0.95}\text{Ni}_{0.05})_2\text{As}_2$ (Ref. 3) compounds. All of these studies have observed the opening of a gap in the spin-fluctuation spectrum and the development of a resonant spin excitation at energies that scale with the superconducting transition temperature, T_c . The intensity of this resonance evolves as a power law below T_c , a situation that is highly reminiscent of the high T_c cuprate superconductors where it is widely held that spin fluctuations are strongly coupled to the superconducting order parameter. In light of recent transport measurements that show that, under hydrostatic pressure conditions, the cT phase itself does not support bulk superconductivity, the observed suppression or absence of both static antiferromagnetic order and dynamic spin fluctuations in the cT phase of CaFe_2As_2 lends support to the notion that spin fluctuations play a role for iron arsenide superconductivity as well.

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