Simultaneous optimization of spin fluctuations and superconductivity under pressure in an iron-based superconductor

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We present a high-pressure NMR study of the overdoped iron pnictide superconductor NaFeO$_{0.94}$Co$_{0.06}$As. The normal-state low-energy spin fluctuations, manifest as the Curie-Weiss upturn in the spin-lattice relaxation rate $1/T_1T$, first increase strongly with pressure but fall again at $p > p_{\text{opt}} = 2.2$ GPa. Neither antiferromagnetic long-range order nor the structural phase transition is encountered up to 2.5 GPa. The superconducting transition temperature $T_c$ shows a pressure-dependence identical to the spin fluctuations, also rising to a maximum at $p_{\text{opt}}$ before decreasing beyond this. Our observations demonstrate that, when extraneous ordering processes are avoided, magnetic correlations and superconductivity are optimized simultaneously as a function of the electronic structure, thereby supporting very strongly a magnetic origin of superconductivity.

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In the iron-based superconductors [1,4], charged dopants usually act to suppress an orthorhombic ground state with antiferromagnetic long-range order (AFLRO) in favor of a tetragonal, paramagnetic, and superconducting phase. Multiple electron bands, which may be formed from all five Fe $d$-orbitals, are observed at the Fermi surfaces [5,6]. These results indicate complex correlation effects involving different electronic degrees of freedom, both orbital and magnetic, in the fluctuations and candidate broken-symmetry phases, which to date have obscured the pairing mechanism for high-temperature superconductivity [7]. While spin fluctuations, usually observed in and around the superconducting phase, are a common candidate for mediating a pairing interaction, it has also been proposed that orbital fluctuations play this role [8]. Direct evidence for the pairing mechanism continues to be the primary goal of the many studies seeking to identify the role of the lattice structure, band structure, and magnetism in determining the superconducting properties.

An applied pressure is well recognized as a particularly clean method for controlling the physical properties of iron-based superconductors. The superconducting transition temperature $T_c$ has been found to change strongly with pressure in LaFeAsO$_{1-x}$F$_x$ (1111 structure) [9], BaFe$_2$(As$_{1-x}$P)$_x$ (122 structure) [10], NaFe$_{1-x}$Co$_x$As (111 structure) [11], Fe$_{1+y}$Se (11 structure) [12], and many other systems [13]. To date, NaFe$_{1-x}$Co$_x$As has shown the most marked effects, even of rather moderate pressures, in its structural, magnetic, and superconducting properties. NMR studies of the parent compound NaFeAs show that the Néel temperature $T_N$ increases with pressure up to 2.4 GPa [14], and x-ray measurements find a collapsed tetragonal phase above 3 GPa [15]. These observations leave open the question of how the changes in $T_c$ may be associated with competing spin fluctuations, AFLRO, and/or changes to the crystal structure, and suggest a systematic study of correlation effects and the pairing mechanism by changing the lattice parameters under pressure.

In this letter, we present a high-pressure $^{75}$As NMR study on the iron-based superconductor NaFe$_{1-x}$Co$_x$As with $x = 0.06$, an overdoping that allows us to avoid both the structural and magnetic phase transitions. In the normal state, the spin-lattice relaxation rate $1/T_1$ first grows significantly with pressure, showing a low-temperature Curie-Weiss upturn indicative of strongly enhanced low-energy spin fluctuations. However, $1/T_1$ then reaches a maximum at $p_{\text{opt}} \approx 2.17$ GPa before decreasing again, a non-monotonic pressure-dependence of the spin fluctuations not previously observed in iron-based superconductors. The superconducting transition temperature has an identical “dome” feature as a function of the pressure, with a maximal $T_c$ at the same $p_{\text{opt}}$. These observations indicate clearly the presence of strong correlations between the magnetism, the superconductivity, and the details of the underlying lattice, are quite different from the effects of doping, and give strong support for a magnetic origin of superconductivity.

NaFe$_{1-x}$Co$_x$As is optimally doped at $x = 0.03$, where the maximal $T_c$ is approximately 20 K [16]. We perform a systematic study of continuous pressure effects on the structure and the magnetic fluctuations, and of how these are correlated with superconductivity, by avoiding both the structural and magnetic phase transitions; for this we focus on a sample with significant overdoping, $x = 0.06$. 

where $T_c \approx 18$ K. The NaFe$_{0.94}$Co$_{0.06}$As single crystals were synthesized by the flux-grown method with NaAs as the flux. The doping level was determined accurately from inductively coupled plasma atomic emission spectroscopy measurements. We used a clamp-type pressure cell, which is limited to 2.5 GPa at low temperatures, for our high-pressure NMR measurements, and Daphne oil as the pressure medium to achieve high pressure homogeneity. As the manometer we used Cu$_2$O, whose nuclear quadrupole resonance (NQR) frequency is known very accurately [17], to calibrate the pressure at different temperatures. The superconducting transition under pressure was determined consistently by NMR and also from the a.c. susceptibility (as described below). The $^{75}$As NMR spectra were obtained by the spin-echo technique under a field of 7.63 T applied in the ab-plane. The spin-lattice relaxation rate $1/T_1$ was measured by the spin-inversion method.

$T_c$ can be determined accurately in situ at all pressures by the a.c. inductance change of the sample coil during cooling and warming at zero field. As shown in the main panel of Fig. 1 the superconducting transition is indicated by an increase in the resonance frequency of the NMR circuit, which measures the a.c. susceptibility, upon cooling. Here we define the onset ($T_c^{\text{onset}}$) and midpoint ($T_c^{\text{m}}$) temperatures from the frequency curve, as illustrated in Fig. 1. Both $T_c^{\text{onset}}$ and $T_c^{\text{m}}$, shown in the inset of Fig. 1, have a strong initial increase with pressure, at a rate of approximately 6 K/GPa. However, after reaching maximal values of 29.8 K ($T_c^{\text{onset}}$) and 27.4 K ($T_c^{\text{m}}$) at a pressure $p_{\text{opt}} \simeq 2.17$ GPa, both quantities then decrease slowly ($-0.6$ K/GPa) at higher pressures. This dome-shaped feature of the superconducting transition is consistent with the results of high-pressure transport studies [11].

We turn now to the NMR data. We have measured $^{75}$As ($S = 3/2$) NMR spectra over the full temperature range to 200 K, at a number of different pressures and with the field applied in the ab-plane. Figure 2(a) shows the center line of the spectrum at $T = 30$ K for several values of the pressure. The spectra shift monotonically to higher frequencies, primarily as a result of second-order corrections to the $^{75}$As quadrupole frequency, $\nu_q$, which we discuss below. The NMR line width increases from 25 kHz at $p = 0$ to 50 kHz at $p = 2.46$ GPa, showing a weak pressure inhomogeneity at higher pressures.

The quadrupole frequency is measured from the $^{75}$As satellite spectra (data not shown). As shown in Fig. 2(b), the low-temperature values of $\nu_q$ display an appreciable rise with pressure up to 2.46 GPa. $\nu_q$ measures the local electric field gradient (EFG), which is very sensitive to the lattice parameters. Such a continuous increase of $\nu_q$ indicates a continuous lattice compression under pressure; neither the line shape nor the frequency of the satellite shows any abrupt changes with temperature or with pressure. This indicates that the structure remains tetragonal and excludes any type of transition to an orthorhombic or collapsed tetragonal structure up to 2.46 GPa, in contrast to the behavior observed in NaFeAs under pressure [14, 15].

The in-plane Knight shift $^{75}K_{ab}$ deduced from the center line of the NMR spectrum is shown as a function of temperature in Fig. 2(c). At a fixed pressure, $^{75}K_{ab}$ increases monotonically with temperature; the functional form $^{75}K_{ab} = A_0 + B_0 T + C_0 T^2$ is characteristic of additive contributions from itinerant electrons ($A_0$) and from predominantly two-dimensional (2D) local spin fluctua-
tions \((B_0)\) [18], with only weak contributions from interplane coupling \((C_0)\). There are no abrupt changes in the Knight shift, which taken together with the absence of diverging behavior in \(1/\tau^\text{Cu} \) above \(T_e\) (shown below) excludes the possibility of any type of magnetic ordering transition up to 2.46 GPa. At a fixed temperature \(T > T_c\), \(75\,K_{ab}\) decreases with pressure. At \(T < T_c\), \(75\,K_{ab}\) drops sharply, which is consistent with a singlet superconducting order parameter. We note that the values of \(T_c\) determined from the Knight shift are consistent with those from the a.c. susceptibility data (Fig. 1).

The \(75\,\text{As}\) spin-lattice relaxation rates \(1/\tau^\text{Cu}\) measured at each pressure are shown in Fig. 3 (a) as functions of temperature up to 200 K. On cooling, \(1/\tau^\text{Cu}\) first decreases with temperature, but then shows a broad, low-temperature upturn before falling abruptly below \(T_c\). This upturn, which becomes increasingly prominent at high pressures, can be fitted rather well by the expression \(1/\tau^\text{Cu}\) \(= A_1/(T - \theta) + B_1 T + C_1 T^2\). This Curie-Weiss form is consistent with 2D low-energy spin fluctuations [19], and suggests their increasing importance as pressure drives the system closer to a magnetic ordering transition. However, unlike the case of underdoped NaFe\(_1-x\)Co\(_x\)As, where \(1/\tau^\text{Cu}\) diverges at a finite temperature due to the onset of AFLRO [14, 20], our overdoped sample shows no divergence and no magnetic order. Instead, the values of \(\theta\) extracted from the fit at each pressure, shown in Fig. 3 (b), approach the divergent regime but then increase again. We draw attention to the fact that \(1/\tau^\text{Cu}\) at low temperatures shows the same non-monotonic pressure-dependence as \(T_c\), first increasing with pressure up to 2.17 GPa but falling beyond this [Fig. 3 (c)]. Thus the low-energy spin fluctuations are optimized at the same pressure \(p_{opt}\) as the superconducting transition temperature. This behavior is also reflected in the maximum of \(\theta\) as a function of pressure [Fig. 3 (b)], which maximizes the Curie-Weiss term.

We conclude our data analysis by performing a detailed comparison between \(T_c\) and the low-energy spin-fluctuation contribution to \(1/\tau^\text{Cu}\). Figure 4 shows \(1/\tau^\text{Cu}\) at \(T = 30\,K\), directly above \(T_c\), and \(T_{cm}\) taken from Fig. 1 for all of the measured pressure values. The two quantities have an initial linear increase with pressure, begin to flatten above 1.7 GPa, are maximal at 2.17 GPa, and fall again at higher pressures. To our knowledge, such a simultaneous optimization of \(T_c\) and the low-energy spin fluctuations in an unconventional superconductor has not been demonstrated before. We have achieved this optimization through the pressure-dependence of both quantities while avoiding both structural and magnetic phase transitions. To make the relationship between the magnetic fluctuations and superconductivity yet more explicit, in the inset of Fig. 4 we plot \(1/\tau^\text{Cu}\) \(= 30\,K\) against \(T_c\) with pressure as the implicit parameter. Pressure-induced changes in both quantities, \(\Delta(T_e)\) and \(\Delta(1/\tau^\text{Cu})\), show a simple linear scaling behavior, which is valid both below and above the optimal pressure.

We begin our discussion by considering the low-energy spin fluctuations. Irrespective of the connection to superconductivity, such an optimization of spin fluctuations by changing the lattice structure (the effect of the applied pressure) has also not been observed previously. Such a non-monotonic change in spin-fluctuation effects clearly

![FIG. 3: (color online) (a) Temperature-dependence of \(1/\tau^\text{Cu}\) at different pressures. The solid lines are fits to the function \(1/\tau^\text{Cu}\) \(= A_1/(T - \theta) + B_1 T + C_1 T^2\). (b) Pressure-dependence of the Curie-Weiss temperature \(\theta\) extracted from the fits in panel (a). (c) Comparison of \(1/\tau^\text{Cu}\) data near \(T_c\) at the two highest pressures [data and fitting lines as in panel (a)].](image1)

![FIG. 4: (color online) Main panel: mid-point superconducting transition temperature \(T_{cm}\) (squares) and normal-state spin-lattice relaxation rate \(1/\tau^\text{Cu}\) at \(T = 30\,K\) (diamonds) as a function of pressure. Inset: scaling between \(T_c\) and normal-state \(1/\tau^\text{Cu}\).](image2)
cannot be described as any sort of effective (negative) doping, as doping leads always to AFLRO in these systems. This type of behavior also contrasts strongly with the effects of pressure in FeSe, where spin fluctuations increase monotonically until AFLRO sets in \[12\].

Because the spin fluctuations can be optimized by pressure but without a change of structure, our results indicate that the magnetic interactions are extremely sensitive to the detailed lattice parameters, and therefore supply information important for a microscopic model. While the iron-based superconductors have a complex, multi-orbital electronic structure, the Fermi surfaces of NaFe\(_{1-x}\)Co\(_x\)As and their orbital nature have been well characterized by Angle Resolved Photoemission Spectroscopy (ARPES) studies \[5, 6, 21\]. NaFe\(_{1-x}\)Co\(_x\)As is a quasi-2D system with weak interlayer coupling, whose band structure is found to be only weakly dispersive along the c-axis. Under these circumstances, one expects that the primary effect of an applied pressure will be to compress the c-axis lattice parameter; this interpretation is consistent with the large but continuous increase of \(75v_{yz}\) \(\text{[Fig. 2(b)]}\), which is determined by \(V_{xz}\), the principal EFG in the tetragonal phase. Because the As sites lie above and below the Fe layers, c-axis compression increases the overlap between the Fe \(dz^2\) and \(d_{yz}\)-orbitals and the As p-orbitals (which also increases the interactions between next-neighbor Fe atoms). This suggests that the pressure-enhanced low-energy spin fluctuations may be associated with an improved Fermi surface nesting of the \(dx^2\) and \(dy^2\) Fe orbitals. Indeed, a recent study combining ARPES and NMR measurements on NaFe\(_{1-x}\)Co\(_x\)As did reveal just such a connection between spin fluctuations and the \(dx^2\) and \(dy^2\) orbitals \[6\].

However, the decrease in spin fluctuations beyond \(p_{opt}\) raises further questions. High-pressure synchrotron x-ray powder diffraction studies of NaFeAs have found that the FeAs planes achieve a structure where the FeAs\(_4\) tetrahedra are completely regular (all internal angles equal to 109.4°) at approximately 3 GPa \[15\]. This regular structure appears to optimize the superconducting transition temperature in many iron pnictides \[22, 23\]. Although we cannot probe the lattice structure by NMR, our results for Co-doped NaFeAs certainly display a similar optimization behavior as a function of the lattice distortion, presumably as the “horizontal” and “vertical” As-Fe-As bond angles approach the regular value from opposite directions under pressure. Our data therefore imply that the connection between the empirical observation of a maximal \(T_c\) and the achievement of a completely regular geometry of the FeAs\(_4\) tetrahedra \[22, 23\] is through the mechanism of magnetic correlations. A structural analysis under pressure is required to investigate how the spin fluctuations we observe may depend on the As-Fe-As bond angles.

Considering the spin fluctuations in more detail, our data show that they have two different types in NaFe\(_{1-x}\)Co\(_x\)As. The first type is the low-energy spin fluctuations, responsible for the low-temperature Curie-Weiss upturn in \(1/T_1T\); these are usually observed in compounds with good Fermi-surface nesting \[24\] and are generally thought to be due to itinerant electrons. However, such an upturn is weak in overdoped 1111 materials \[9\], completely absent in the intercalated iron selenide K\(_x\)Fe\(_{2-x}\)Se\(_2\) \[25\], and weak in NaFe\(_{0.94}\)Co\(_{0.06}\)As at ambient pressure \[Fig. 3\], yet all of these systems have a high \(T_c\). To identify the origin of the strong pairing interactions in these compounds, we note that their Knight shifts increase significantly with temperature, as observed respectively in Ref. \[9\], Ref. \[18\], and Fig. \[2\,c\]. This strong thermal enhancement is consistent with fluctuating local moments, rather than with a band-structure effect \[18\]. From our results at different pressures, the low-energy spin fluctuations are strongly enhanced by the pressure \[Fig. 3\], while the local spin fluctuations are strong at low pressures but weaken as \(p\) increases \[Fig. \[2\,c\]\].

Turning now to the connection with superconductivity, the paradigm of a spin-fluctuation-mediated pairing interaction whose strength diverges at the magnetic instability in the random phase approximation (RPA) has long been the foundation for a number of theories of high-temperature superconductors. However, in cuprate materials the separation in doping between the AFLRO phase and the dome-shaped maximum in \(T_c\) is impossible to reproduce in such a scenario. Here we have obtained a direct proof for the correlation between low-energy spin fluctuations and superconductivity by the simultaneous optimization of both, using pressure instead of doping as the control parameter. This is a very strong statement in favor of a magnetic origin for superconductivity. We remind the reader that the pressure-enhanced \(T_c\) we observe is correlated more directly with the low-energy spin fluctuations, which are due to itinerant electrons, than with the local spin fluctuations. This behavior is also manifest in the doping-dependence of the two types of spin fluctuation, where the high-energy ones were found \[20\] to change little with electron doping in BaFe\(_2\)As\(_2\) while, as with the effects of applied pressure, the dominant changes were found in the low-energy ones.

This observation also sheds further light on the question, raised recently by several authors, of whether superconductivity in the iron-based materials requires low-energy spin fluctuations at all, given that these seem to be weak or absent in some systems. We have shown from our ability to monitor how the spin fluctuations evolve with pressure that superconductivity is correlated with two types of spin fluctuation. To distinguish between the contributions of each, we return to the perfectly linear relation between \(T_c\) \(\propto 1/7575T_1T\) and \(T_c\) in the inset of Fig. \[4\] and note that \(T_c\) extrapolates to a finite value (around 8 K) as \(1/7575T_1T \to 0\). This indicates that low-energy spin fluctuations are not the only contribution to the pairing mech-
anism, and that superconductivity may arise in their absence. Given the presence of local spin fluctuations, which are strong at low pressures [Fig. 2(c)], we suggest that these are the short-range magnetic correlation effects providing the additional pairing mechanism, which is dominant in some materials. In NaFe$_{0.94}$Co$_{0.06}$As, our data show that both local and low-energy spin fluctuations contribute to superconductivity at ambient pressure, while the latter dominate at high pressures; this balance of contributions is expected to be different for different sample dopings.

Finally, spin fluctuations are not the only candidate pairing mechanism in Fe superconductors. Theoretical analysis of a five-band model with electron-phonon coupling leads to the proposal of orbital-fluctuation-mediated superconductivity [8]. We turn to the data to resolve this question. Our results are unequivocally in favor of a magnetic origin. Quite apart from the direct correlation of $T_c$ and $1/\sqrt{75}T_1$, phonon-mediated pairing interactions are conventionally expected to increase monotonically with pressure, and so a non-monotonic change in $T_c$ does not appear to be consistent with the orbital-fluctuation scenario. A further consequence of the orbital-fluctuation mechanism is a conventional $s^{++}$ pairing symmetry, which should result in the observation by NMR of a coherence peak robust against disorder. We are also uniquely positioned to comment on the pairing symmetry at all pressures. The spin-lattice relaxation rate also drops sharply below $T_c$ here, and the coherence peak is absent at all pressures. This result indicates an unconventional pairing symmetry such as $s^+$, which is sensitive to impurity scattering, and once again contradicts the orbital-fluctuation prediction. We found no evidence for a change of pairing symmetry under pressure, but cannot exclude a partial contribution from any other mechanism.

In summary, we have demonstrated a direct connection between superconductivity and low-energy spin fluctuations in a high-temperature superconductor. We chose to analyze NaFe$_{0.94}$Co$_{0.06}$As, an overdoped system where both the structural phase transition and antiferromagnetic long-range order are avoided. We performed NMR measurements, which are extremely sensitive to both low-energy and local spin fluctuations, under an applied pressure, which allows clean and detailed control of both the lattice and electronic structures. We show that the spin fluctuations and the superconducting transition temperature change in lockstep, and are optimized at exactly the same pressure. This result strongly supports a magnetic origin for superconductivity. Our measurements also demonstrate the presence of two types of spin fluctuation, namely low-energy ones arising from itinerant electrons and finite-energy ones with a local nature, and that both contribute to pairing in the superconducting state.

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[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[2] G. F. Chen et al., Phys. Rev. Lett. 100, 247002 (2008).
[3] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature 453, 761 (2008).
[4] Z. A. Ren et al., Chinese Phys. Lett. 25, 2215 (2008).
[5] M. Yi et al., New J. Phys. 14, 073019 (2012).
[6] Z. R. Ye et al., arXiv:1303.0682 (2013).
[7] J. Paglione and R. L. Greene, Nature Phys. 6, 645 (2010).
[8] H. Kontani and S. Onari, Phys. Rev. Lett. 104, 157001 (2010).
[9] T. Nakano et al., Phys. Rev. B 81, 100510(R) (2010).
[10] L. E. Klintberg et al., J. Phys. Soc. Jpn. 79, 123706 (2010).
[11] A. F. Wang et al., New J. Phys. 14, 113043 (2012).
[12] T. Imai, K. Ahilan, F. L. Ning, T. M. McQueen, and R. J. Cava, Phys. Rev. Lett. 102, 177005 (2009).
[13] C. Chu and B. Lorenz, Physica C 469, 385 (2009).
[14] L. Ma, G. F. Chen, D. X. Yao, J. Zhang, S. Zhang, T. L. Xia, and W. Yu, Phys. Rev. B 83, 132501 (2011).
[15] Q. Liu et al., J. Am. Chem. Soc. 133, 7892 (2011).
[16] A. F. Wang et al., Phys. Rev. B 85, 224521 (2012).
[17] A. P. Reyes, E. T. Ahrens, R. H. Hefnner, P. C. Hammel, and J. D. Thompson, Rev.Sci. Instrum. 63, 3120 (1992).
[18] L. Ma et al., Phys. Rev. B 84, 220505(R) (2011).
[19] T. Moriya and K. Ueda, Solid State Commun. 15, 169 (1974).
[20] L. Ma et al., (unpublished).
[21] Z.-H. Liu et al., Phys. Rev. B 84, 064519 (2011).
[22] C.-H. Lee et al., J. Phys. Soc. Jpn 77, 083704 (2008).
[23] J. Zhao et al., Nature Mater. 7, 953 (2008).
[24] H. Ding et al., Europhys. Lett. 83, 47001 (2008).
[25] W. Yu et al., Phys. Rev. Lett. 106, 197001 (2011).
[26] M. S. Liu et al., Nature Phys. 8, 376 (2012).
[27] K. Ishida, Y. Nakai, and H. Hosono, J. Phys. Soc. Jpn. 78, 062001 (2009).