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ABSTRACT

We report on systematic temperature and doping dependent measurements of the Fe 3s core level photoemission spectra in the normal state of superconducting $Sr(Fe_{1-x}Co_x)_2As_2$. The analysis of the Fe 3s spectrum provides an element-specific determination of the mean value of the magnitude of the Fe spin moment measured on the fast ($10^{-16} – 10^{-15}$ s) timescale of the photoemission process. The data reveal the ubiquitous presence in the normal state of Fe spin moments with magnitude fluctuating on short time scales.

The data reveal a significant reduction of the magnitude of the effective Fe spin moment on going from the parent to the optimal doped compound. The doping dependence of the magnitude of the spin moment at higher doping level is less clear, being either constant, or even non-monotonic, depending on temperature. This phenomenology indicates the importance of the interaction between spin and itinerant degrees of freedom in shaping the properties of the normal state. These findings reaffirm the complexity of the normal state of 122 Fe-pnictides, which are typically viewed as the least correlated of the high temperature unconventional superconductors.

INTRODUCTION

A correct description of high temperature (high-T_C) superconductivity requires a deep understanding of the normal state from which it emerges. The properties of the normal state include fundamental information on the nature and details of the quasiparticles and their excitation spectra, as well as possible interactions that could give rise to an instability against a superconducting state. A proper understanding of the normal state has been a notoriously challenging task due to varying degrees of electronic correlations and competing orders. This is also the case for iron-based high-T_C superconductors (Fe-HTSC).

High-T_C superconductivity in Fe-HTSC originates from a normal state. Doping via chemical substitutions or insertions strongly affects this state by changing the electron count and is essential for obtaining high T_C in many of the Fe-HTSC. Yet, a proper understanding of doping has proved to be a challenging task even for the pnictide Fe-HTSC, which are in many cases viewed as the least correlated of the high-T_C unconventional superconductors [1,2,3]. This is exemplified by the controversy centered on the role of transition metal substitutions in electron-doping the prototypical 122 pnictide $BaFe_2As_2$ (Ba122) [4,5]. Co-doping was found to induce changes in the Fermi surface consistent with Luttinger's theorem (i.e. the number of doped electrons agrees with the nominal number of extra electrons) [4]. This has helped shape a belief that the electronic structure of Co-doped Ba122 might evolve according to the rigid band model, i.e. the effect of electron and hole doping may be mainly accounted for by raising or lowering the chemical potential, although this is not a direct consequence of Luttinger's theorem, especially in a multiband system. More recently, however, angle resolved photoemission (ARPES) experiments have shown that the validity of the rigid band model is untenable [5]. In fact, the deviations from the prediction of rigid band models are quite significant, as revealed by the highly non-monotonic dependence on Co concentration of key quantities such as band filling, bandwidth of the electron pocket, and quasiparticle coherence [5]. Even for the simplest Co-doped Ba122, the effects of doping in pnictides and the evolution of the electronic properties of the normal state are thus more complicated than initially believed.

In this work, we provide further evidence for the complexity of the normal state in pnictides materials by reporting on the doping and temperature dependence of the Fe 3s photoemission spectra measured in Co-doped $SrFe_2As_2$. The analysis of such spectra provides a direct and element-specific measurement of the magnitude of the effective Fe spin moment measured on the fast ($\approx 10^{-16} - 10^{-15}$ s) time scale typical of the photoemission process. This provides a unique probe for the detection of ultrafast directional and longitudinal spin fluctuations in a material where these are suspected to be crucial for understanding the

normal state properties, and possibly the superconductivity. The magnitude of the Fe spin moment measured in this way exhibits a weak temperature dependence (largest at higher doping levels), while the dependence on doping is more significant. Specifically, the magnitude of the spin moment is substantially ($\approx$ 40%) reduced on going from the parent to optimal doped compound, while from optimal to higher doping levels it either remains constant, or exhibit non-monotonic traits. This phenomenology represents a further challenge for our current understanding of the normal state of pnictide materials.

EXPERIMENTAL

$Sr(Fe_{1-x}Co_x)_2As_2$ single crystals were grown from an FeAs/CoAs flux as described elsewhere [6]. For this study, nominal compositions of x = 0.0, 0.06, 0.12, 0.16, 0.20, and 0.30 gave crystals with actual Co concentrations, x = 0, 0.03, 0.10, 0.13, 0.17, 0.27, as determined with Energy Dispersive Spectroscopy (EDS). The EDS values will be used hereafter to refer to the sample compositions. Characterization measurements were performed on as-grown crystals. Resistivity measurements showed that the undoped (x = 0) and lightly doped (x = 0.03) crystals undergo the well-known magnetic and structural phase transitions at 190 and 120 K, respectively. Only the x = 0.10 and 0.13 samples showed bulk superconductivity as determined by the resistivity measurements. Their superconducting transition temperature T_C, at which the measured resistance was zero, are 12 K and 8 K, respectively. The resistivity of the sample with x = 0.17 showed the onset of a superconducting transition near 4 K, but the transition was not complete at 2 K. No evidence of superconductivity was seen for x = 0.27 down to 2 K. These results are in general agreement with the data and phase diagram reported in Ref. [7]. The x = 0.03 sample is thus underdoped, and will be referred to as "UD_3". The x = 0.10 sample is closest to optimal doping, and will be denoted as "Opt". The samples with x = 0.13, 0.17 and 0.27 are overdoped, and named "OD_{13}", "OD_{17}", "OD_{27}", respectively.

The crystals were cleaved *in-situ* in a pressure better than 3×10^{-11} Torr, at temperature T = 28 K. No ageing effects were detected within a maximum of 24 hours of sample exposure to the photon beam. The photoemission measurements were performed at Beamline 10.0.1 of the Advanced Light Source (ALS). The spectra were excited with photons of 241 eV, with a total instrumental resolution of 100 meV. For each sample, the spectra were recorded at five different temperatures, T = 15 K, 30 K, 90 K, 150 K and 220 K, with the analyzer slit oriented in between the (100) and (110) crystallographic directions.

RESULTS AND DISCUSSION

Fig. 1 shows Fe 3s core level spectra recorded in each sample at different temperatures. The spectra all exhibit doublets due to multiplet splitting (M-SP) of the binding energy (BE), a well-known effect in transition metals [8,9,10], and which has been documented also in Fe-HTSC [11,12,13]. The M-SP arises from the exchange coupling of the core 3s electron left behind upon photoelectron emission with the net spin S_V in the unfilled outer shell(s) of the emitter atom (Fe 3d/4s in this case; we refer to these orbitals as 3d in the following, although there is clearly hybridization both with combinations of pnictogen p and other Fe orbitals, e.g. 4s). The M-SP occurs exclusively in atoms with the outer subshell(s) partially occupied with a non-vanishing net spin S_V, at least on short time scales. The data shown in Fig. 1 thus reveal that, for all of the different Co concentrations, temperatures, and phases accessed in the experiment, the Fe is found to have a non-vanishing net spin S_V originating from partially occupied 3d orbitals. The values of the net spin S_V were extracted from the separation ΔE_{3s} according to a procedure validated for other itinerant systems [11,12,14,15]. The peak separation ΔE_{3s} was determined with two-component fits of the spectra (cf. Fig. 1). The analysis of the Fe 3s spectra leads to the determination of 2S_V, the magnitude of a quantity that, from now on, we refer to as the fluctuating spin moment (FSM). We note that with the exception of the zero and under-doped sample UD$_3$, there are no ordered magnetism and no static moments. The values of the peak separation ΔE_{3s} and the corresponding 2S_V values of the FSM as a function of temperature and Co concentrations are shown in Figs. 2 and 3. The magnitudes of the FSM extracted from Fe 3s PES spectra are found to be considerably larger than the values determined with more conventional magnetic techniques. For the pnictides, this a documented occurrence that originates from the different time-scales of the measuring techniques [13].

Any attempt to formulate a correct interpretation of the data and provide insights into the physics of the pnictides must be preceded by a description of the difference between the nature of the FSM extracted from the data, and the spin moment determined with more conventional magnetic measurements. In a photoemission experiment, the system is sampled over extremely short time scales $\approx 10^{-16} - 10^{-15}$ s. The values S_V extracted from the peak separation ΔE_{3s} are thus representative of the net magnitude of the spin of an Fe atom measured on such short time scales, and averaged over all of the Fe sites. In contrast, conventional magnetic measurements such as Mössbauer, NMR, and μ-SR have characteristic time scales $\approx 10^{-8}$ s – 10^{-6} s, practically static compared to the time scale of PES. In itinerant systems, the values of the spin moment determined with different techniques can be very sensitive to the time scales involved in the measurement. The discrepancy in the magnitude of the spin moment between the fast ($\approx 10^{-16} - 10^{-15}$ s) and slow (10^{-8} s - 10^{-6} s) measurements is due largely to the occurrence of quantum fluctuations, to which only fast measurements are sensitive. The term "quantum fluctuations" denotes the very fast fluctuations

of the amplitude of the spin moment occurring exclusively in itinerant systems [16,17]. If W denotes the bandwidth, itinerant electron systems are characterized by a fundamental timescale $\tau_F \approx h/W = \approx 10^{-15}$ s characteristic of electron dynamics. Itinerant electrons have wavefunctions which are phase-coherent over large distances, with the result that the electron density, and as a consequence the spin density, are not fully described by sharp atomic-like quantum numbers. On timescales $\approx \tau_F$, the magnitude of the spin moment exhibits very fast fluctuations (i.e., the *quantum fluctuations*), with a mean value of $2S_V$.

Conventional magnetic experiments probe the system on timescales much longer than τ_F. Consequently, they average over the quantum fluctuations, and detect values for the magnitude $2S_V$ that can be considerably smaller than those determined with fast ($\approx \tau_F$) experiments such as PES and x-ray emission spectroscopy (XES), as in the case of the pnictides [12,13,18,19]. The FSM is in general also larger than the spin moment extracted from inelastic neutron scattering, which is a fast experiment, albeit not as fast as PES and XES [13]. Quantum fluctuations are longitudinal spin fluctuations, i.e. they feature different values of the amplitudes $2S_V$ of the spin moment, and are markedly different from transversal spin fluctuations. The latter denote the orientation fluctuations of the spin moment after being averaged over the fast quantum fluctuations. The transversal fluctuations are observed for example as the fluctuations of local moments in paramagnetic phases, or in spin waves, which consist in a wave-like precession of the averaged moment occurring on timescales $\approx 10^{-13}$ s, much slower than the fast τ_F [13,16].

The values $2S_V$ extracted from the Fe 3s PES spectra are thus representative of the magnitude of the FSM, i.e. a quantity identified with a spin moment sampled on timescales shorter than, or at most comparable to, the timescales $\approx \tau_F$ associated with the quantum fluctuations, and averaged over all of the Fe sites. Although the timescales are very short, the values of the FSM revealed by the M-SP are meaningful, as they provide a quantitative estimate of the spin moments that the itinerant electrons interact with self-consistently on a timescale relevant to their dynamics. This type of interaction is expected in 3d itinerant magnetic systems, as in this case a clean separation of magnetic and itinerant degrees of freedom does not occur [20,21,22]: since the magnetism stems from electrons which also happen to participate in the Fermi surface, it is not clear to what degree it is possible to separate itinerant and localized electrons. This is the reason why, although the M-SP arises from an on-site exchange interaction, we refer to the values $2S_V$ extracted from the M-SP of the Fe 3s spectra as FSM's, rather than local moments, to emphasize that the Fe 3d bands are itinerant, and not localized [23]. The FSMs are akin to exchange fields located at Fe atoms, and varying from atom to atom [20,21]. The motion of the itinerant electrons and the FSM's are influenced reciprocally in a self-consistent fashion, much like the electrons would interact with fast changing exchange fields, varying from atom to atom, resulting in different configurations of the

exchange fields readjusting on timescales $\approx \tau_F$. Because of the intrinsic fast timescale of the measurement, an Fe 3s PES spectrum is essentially equivalent to a snapshot of the system, and reflects the distribution of different FSM's at different sites. As previously documented, the best fits to the Fe 3s spectra are always obtained when the curve fitting the peak at higher BE is mainly of Gaussian character, with a width much larger than that of the lower BE peak, and that expected from experimental resolution [11,12,13]. Indeed, fluctuations in the amplitude of the spin moment on Fe sites should appear in an Fe 3s spectrum as sidebands at higher BE with the peaks envelope being a Gaussian, reflecting the normal character of their distribution, and the fact that S_V is not a good quantum number [24]. In the spirit of an ergodic argument, we can also infer that the Fe 3s PES spectrum, which reflects the statistical distribution of different FSMs at different sites, is also representative of the sampling of a single spin moment at a random site fluctuating on time scales $\approx \tau_F$ with mean value $2S_V$.

The values of the peaks separation ΔE_{3s} and the corresponding $2S_V$ mean values of the FSM as a function of temperature for different Co concentrations are shown in Fig. 2. The different ranges of the values on the vertical axes indicate that the variation of the FSM with temperature for the P, UD_3, and Opt compounds is almost completely within the error bars, but it becomes progressively more significant in the OD regime, reaching a maximum (≈ 0.5 μ_B) in the OD_{27} sample. The most significant finding revealed by our data is the doping dependence of the FSM against Co concentration, shown in Fig. 3 for different temperatures. For all the temperatures accessed in the experiment, the FSM is maximum in the P compound, and decreases monotonically up to Opt. doping. The reduction of the FSM from the parent to the Opt. doped compound is quite substantial (40 – 45%), in agreement with our previous studies [12]. From Opt. doping to higher doping levels, the value of the FSM does not decrease any longer. For the T = 15 k data, the magnitude of the FSM is constant, within the error bar. For all of the other temperatures (T = 30, 90, 150, and 220 K), however, the doping dependence is overall unclear. The value of the OD_{13} sample is higher than that of the Opt. doped sample by more than two (T = 90 K), or even three standard deviations (σ). It is also higher than that of the OD_{17} sample by at least two σ's (T = 30, 90, and 220 K), and > 3 σ's for the data taken at T = 150 K. The OD_{13} sample exhibits therefore a local maximum. A more detailed study with samples of different doping close to OD_{13} would be necessary to establish whether the data exhibit any oscillatory behavior in this doping range. The OD_{27} sample exhibits a value of the FSM that is comparable (within the error bar) to that of the Opt. doped compound for the data taken at 90 K and 150 K. For the data taken at T = 30 and 220 K, however, the value of the FSM for the OD_{27} sample is essentially the same as that of the UD_3 sample, and higher (within 3 σ's) that the value of the Opt. doped sample.

The phenomenology shown in Fig. 3 is not obvious. The data are not compatible with an exclusively local nature of the FSM's. As already observed in previous work, the strong reduction of the FSM's between the parent and the Opt compound cannot be accounted for by changes of the local properties of the Fe ion due to electron filling of the Fe 3d orbitals upon increasing Co concentration [12]. As evidenced by the relation between the multiplet separation ΔE_{3s} and the magnitude $2S_V$ of the FSM, i.e. $\Delta E_{3s} = 0.94 + 1.01 \times (2S_V + 1)$ (cf. Fig. 2), one would expect a linear relationship between the separation ΔE_{3s} and Co concentration, given that S_V would scale linearly with the number x of electrons introduced with Co substitution, under the hypothesis that such charge were completely donated to Fe. Clearly the drastic $\approx 40\%$ reduction of the FSM on going from the parent to the Opt doped compound does not support this scenario. This is irrespective of the spin configuration of the Fe d^6 ion. Co substitution would linearly decrease the value of S_V if the Fe d^6 ion adopted a high spin configuration ($2e_g^\uparrow 3t_{2g}^\uparrow 1e_g^\downarrow$, $S_V = 2$), and increase it if the Fe d^6 ion adopted a low spin configuration ($2e_g^\uparrow 2 e_g^\downarrow 2t_{2g}^\uparrow$, $S_V = 1$). All of the measurements of the FSM in the parent compound and the DFT predictions are, however, more consistent with the value $S_V = 1$ [13], and thus the multiplet separation ΔE_{3s} should increase with Co substitution, while it clearly does not, at least from P to Opt. doping. This may be simply a consequence of the itinerant nature of the electronic system.

The strong reduction of the FSM between the parent and the Opt compound reveals instead the importance of the reciprocal, self-consistent interaction of itinerant electrons with the FSM, i.e. exchange field at a particular atomic site sampled on fast timescales ($\approx 10^{-16} – 10^{-15}$ s) [12,13]. Nonetheless, even in this case, i.e. when considering the electron itinerancy contribution to the formation of the FSM, the doping dependence of the data shown in Fig. 3 is still not obvious. Usually M-SP observed spectroscopically in the Fe 3s PES spectra correlate with the magnitude of the atomic spin moments of Fe atoms that are magnetic, as found in both ordered and paramagnetic phases. It is also observed, however, in "non-magnetic" atoms as found in materials that, according to the results of conventional magnetic measurements such as magnetic susceptibility, neutron diffraction, Mössbauer, NMR and μ-SR, do not show either any magnetic order, or any Fe spin moment component of the Curie-Weiss moment. For example, Fe compounds such as FeAl, NbFe$_2$, and YFe$_2$Ge$_2$ are all characterized by strong spin fluctuations, the presence of itinerant electrons, and strong dependence of transport and other properties on temperature [25,26,27,28]. All show evidence of nearness to a magnetic quantum critical point, and YFe$_2$Ge$_2$ is also a superconductor [29]. The connection between the normal states of the Fe-pnictide superconductors and metallic YFe$_2$Ge$_2$ has recently been discussed in detail [28]. In these systems, the observation of M-SP in the Fe 3s PES spectra indicates the occurrence of fast fluctuations of the spin

moment, whose detection is possible due to the fast timescale of the measurement, as discussed above. The M-SP of the Fe 3s spectra and the extracted values of the FSM reported here can be associated with large magnetic fluctuations, analogous to those exhibited by itinerant systems near quantum critical points.

The Fe-pnictide phase diagrams generally show the highest ordering temperatures and strongest antiferromagnetism without doping, corresponding to the composition $SrFe_2As_2$. The antiferromagnetic ordering is suppressed with doping, and a superconducting dome appears. At low doping there is a magnetic phase transition, and therefore thermal fluctuations near the ordering temperature should be present. While thermal fluctuations near a phase transition may be large, they also tend to be fluctuations of low energy degrees of freedom. For example, when approaching a second order magnetic ordering transition from below, spin fluctuations associated with soft spin waves increase in amplitude as the spin wave energy goes to zero at the transition. In contrast, our data are consistent with the amplitude of the spin fluctuations increasing to high energy, even at room temperature. Interestingly, according to our measurements, the FSM does not change strongly with temperature in the undoped to optimally doped region, even going through the transition temperature at zero doping. This is in contrast to low energy properties such as transport and NMR Knight shift, but is more in line with the high energy spin fluctuations measured by neutron scattering. In the Fe-pnictides, dispersing spin fluctuations are seen up to at least 200 meV [30]. The temperature dependence is stronger for the overdoped samples, possibly consistent with the character of the spin fluctuations changing beyond optimal doping [31]. The value of the FSM's, which represent the mean size of the amplitude fluctuations, increases as one moves towards and into the magnetically ordered region at low Co concentrations. Within this scenario of FSM being directly associated to magnetic fluctuations, however, it is not obvious why the FSM does not further decrease for higher Co concentrations, i.e. moving away from the magnetically ordered state. In fact, from Opt. doping to higher doping levels, the value of the FSM does not decrease any longer, and it is even higher than the Opt. doped value for some temperatures.

The reduction in magnitude of the FSM is also consistent with a delocalization of the 3d orbitals [12]. The M-SP is proportional to the exchange integral $K_{3s,VS}$ between the 3s core level and the unfilled 3d orbitals, and is thus sensitive to the spatial overlap of their wavefunctions. Lower values of the multiplet separation ΔE_{3s} in the Fe 3s core level spectra thus may indicate a reduction of the overlap between the core Fe 3s and the itinerant 3d electron orbitals, in addition to changes in the magnitude of the FSM. Given the localized character of the Fe core 3s wavefunction, lower values of the FSM are consistent with a more spatially delocalized character of the itinerant 3d electron orbitals [12]. The data shown in Fig. 3 indicate that, for all points in the normal state of the phase diagram accessed by the experiment, the

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magnitude of the FSM decreases by ca. 40% from the P to Opt. doping, and then it either stays constant (for the T = 90 and 150 K data), or even increases in the OD_{27} sample (for the T = 30 and 220 K). It cannot be stated that the FSM is minimum for Opt. doping with a confidence better than one σ. It is true, however, that the FSM for the Opt. doped sample has a lower value than in the P and UD_3 samples with a confidence of at least two σ's (for the T = 15, 90, and 220 K data), and even three σ's (for the T = 30 and 150 K data), suggesting a more delocalized character of the itinerant 3d electron orbitals in the Opt. doped sample. Interestingly, the delocalization of the 3d wavefunctions in proximity of optimal doping is fully consistent with ARPES data in Co-doped $BaFe_2As_2$, which indicate that at optimal doping the spectral features for states at the Fermi level with in-plane character become sharper, i.e. more coherent [5]. It is interesting to note that the sharpening of the in-plane states is non-monotonic, as the effect is most pronounced at optimal doping [5]. Given the similarity between the Ba122 and Sr122 systems, it is natural to think that such effects might also correlate with the doping dependence of the FSM reported here. Similar considerations can be given to describe the occurrence of the local maximum in the OD13 sample for temperatures T ≥ 30 K. The latter is certainly intriguing, given that in the Sr122 system the phase diagram to the right of optimal doping does not show either phase boundaries, or anomalies [7]. Nonetheless, the non-monotonicity of some of the data here discussed is not so surprising in light of the complicated doping dependence found in the Ba122 system [5]. For example, ARPES data in Co-doped $BaFe_2As_2$ have exposed significant non-monotonic changes in proximity to optimal doping of key features such as the Fermi crossing of bands with different orbital symmetry, and the bandwidth of the electron pocket. Given that in a 3d itinerant system the moment is formed also by the same electrons forming the Fermi surface, it is natural to think that also the FSM's exhibit changes with Co concentration that defy simple explanations.

The drastic ≈ 40% reduction of the FSM on going from the parent to the Opt doped excludes an exclusively local nature of the FSM's, and corroborates instead the importance of electron itinerancy for both the formation of, and the interactions with the FSM's on the fast time scales of the photoemission experiment. We have also discussed how the FSM's can be associated with large magnetic fluctuations, analogous to those exhibited by itinerant systems near quantum critical points, and how the reduction of the FSM on going from the parent to the Opt. doped compound is also consistent with a delocalization of the 3d orbitals. The data and the relative observations reported above indicate that the dependence of the FSM on Co concentration is certainly not trivial. This conclusion, which is the main result of this work, is particularly compelling in light of the fact that 122 Fe-pnictides are typically viewed as the least correlated of the high temperature unconventional superconductors. Yet, these findings contribute to assert the

complexity of the normal state of 122 Fe-pnictides by showing that the doping dependence of the FSM defies simple explanations.

At this stage, we can only speculate on the occurrence of some mechanism at work behind the complexity of the normal state of pnictides that are compatible with the findings presented here. If the FSM's are associated with large magnetic fluctuations, analogous to those exhibited by itinerant systems near quantum critical points, then the fact that for Co concentrations higher than Opt doping the value of the FSM does not decrease any longer, but it even increases for some temperatures, suggests the presence of another ordered magnetic state that is approached at high Co concentration. If correct, this interpretation of the data would suggest that the superconducting state in pnictides is associated with a strongly spin fluctuating metal influenced by two quantum critical points in the phase diagram. The competition between magnetic states seems to be an indicator of materials with large quantum critical regions, as for example the ruthenates [32], suggesting that the pnictides are materials strongly influenced by quantum criticality.

Focusing instead on the correlation between the lower values of the FSM's and delocalization of the 3d orbitals, the data are consistent with the identification of the competition between the kinetic energy of the itinerant electrons and the antiferromagnetic correlations of the FSM's as the driving factor shaping the physics of the pnictides. As also emphasized in previous studies, the reciprocal, self-consistent interaction between itinerant electrons and FSMs is of fundamental importance for shaping the magnetism in pnictide materials [12,13,33]. This interaction has been modeled on the basis of spin-fermion models [33,34,35]. The essence of spin-fermion models consists in partitioning local and itinerant degrees of freedom, and consider local moments interacting antiferromagnetically with each other, and ferromagnetically with itinerant electrons (Hund's coupling). This approach highlights the perspective of the locally ordered state, stemming from the strong short-range antiferromagnetic correlations among the moments, and considers the effect of quantum fluctuation on the strength of this local order. Recent work has described in detail how itinerant carriers, together with deviation from perfect nesting of the Fermi surface, induce spatial and temporal quantum fluctuations, leading to a reduction of the ordered moment [33]. Certainly our data confirm the important role played by the itinerant electrons in shaping the magnetism of pnictide materials via self-consistent interaction with the FSMs, i.e. the exchange field on each site. Previous data exposed a reduction of the FSM's between parent and Opt doping, and were deemed to be suggestive of strong competition between the antiferromagnetic super-exchange interactions among the FSM's, and the kinetic energy gain of the itinerant electrons in the presence of a strong Hund's coupling [12]. This view is still consistent with the new data reported here: minimization of the kinetic energy due to the increase of

itinerancy increases the quantum fluctuation, reduces the moment correlation length, and increases the fluctuations of the FSM, which is detected to be smaller upon averaging over the short timescale of the PES measurement. The validity of this argument would identify the minimization of the kinetic energy as the driving force behind the observed phenomenology. Interestingly, the increased sharpness of the spectral features at the Fermi level observed for states with in-plane character at optimal doping, i.e. more coherent states, in the closely related Ba122 system is consistent with minimization of the kinetic energy. If this scenario were correct, one could speculate that superconductivity, or at least the critical temperature, benefits directly from kinetic energy minimization. This would suggest that superconductivity in pnictides could be drastically different from the pairing strength dominant picture, and more in line with a kinetic energy driven mechanism. Further experiments are clearly needed to validate this scenario.

Ultimately, much of the intrinsic difficulty in proposing a unique microscopic mechanism responsible for the observed phenomenology stems from different possible ways of describing the Fe 3d bands. Different theoretical approaches ascribe different degree of localization to the different d bands, leading to possible different interpretations of the experimental results. It is also to be noted that the specific ordering patterns of Fe orbitals and momentum dependent low energy spin fluctuations from neutron scattering, are consistent with a strong influence of the Fermi surface with itinerancy of the magnetism, as opposed to dominant superexchange interactions between localized moments. Our data, representative of sub-picosecond time scales, show unambiguously that the FSM's do not consist of localized states, at least exclusively, and reveal instead the importance of the reciprocal, self-consistent interaction of itinerant electrons with the FSM's. Yet, on the basis of the data, whether the FSM's are formed exclusively from itinerant states or encompass also a portion of localized states remains unclear. Further experiments are clearly needed in order to sort this out at different energy and time scales, and to elucidate the mechanisms responsible for the drastic reduction of the spin moments when measured on long time scales.

CONCLUSIONS

We have studied the doping dependence of the Fe 3s core level photoemission spectra in the normal state of $Sr(Fe_{1-x}Co_x)_2As_2$ pnictide high-T_C superconductors. The analysis of the spectra allows the determination of the mean value of the magnitude of the Fe spin moment measured on the fast ($10^{-16} – 10^{-15}$ s) time scale typical of the photoemission process, and averaged over all of the Fe sites. The substantial reduction of the magnitude of the spin moment from the parent to the optimally doped compound reaffirms the importance of the contribution of itinerant electrons in shaping the spin moments on the short timescales of electron dynamics [12]. The doping dependence for higher doping levels is less clear, being

either constant, or even non-monotonic, depending on temperature. Taken together with the inapplicability of the rigid band model, and the non-trivial dependence upon doping of key quantities such as band filling, bandwidth of the electron pocket, and quasiparticle coherence observed in Co-doped Ba122, the non-monotonic variation upon doping of the amplitude of the spin moment in Sr 122 discussed here reaffirm the complexity of the normal state in Fe pnictide materials [5].

FIGURE CAPTIONS

  Fig. 1.   (color online) Multiplet splittings in Fe 3s core level PES spectra: evidence of fluctuating spin moments on the Fe sites.   Fe 3s core level PES spectra in $Sr(Co_xFe_{1-x})_2As_2$ recorded for different Co concentrations and different temperatures. A Shirley-type background has been subtracted from the data points (circles). The M-SP of the BE is clearly visible as a doublet structure consisting of a main line and a satellite peak at higher BE. The continuous line through the data points is the result of the two component fit of the doublet. The distance between these two peaks maxima provides the multiplet separation ΔE_{3s}, with experimental uncertainty on ΔE_{3s} of $\pm$ 150 meV.

  Fig. 2.   (color online) Multiplet energy separation ΔE_{3s} and FSMs. Values for the multiplet energy separation ΔE_{3s} (squares) as a function of temperature for different Co concentrations. The values of the FSMs (circles) have been extracted from the multiplet separation ΔE_{3s} via the relation *$\Delta E_{3s} = 0.94 + 1.01 \times (2S_V + 1)$* [11]. For clarity, the error bars are shown for all point for the FSM, but only for one point for the multiplet separation ΔE_{3s}. The uncertainties on the determination of the multiplet separation ΔE_{3s} and the FSM *$2S_V$* are $\pm$ 150 meV and 0.15 μ_B, respectively. The data indicate that the temperature dependence of the magnitude of the FSM is more pronounced in the OD_{17} and OD_{27} samples.

  Fig. 3.   (color online) Dependence of the FSM on Co concentration. The dependence of the FSM on Co concentration plotted for different temperatures. The FSM has minimum values in correspondence of optimal doping.

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[23] The term local moment used in our previous study [12] coincides with the notion of FSM used here. FSM's are "local" in the sense that are located on Fe sites, but not exclusively formed by localized states.

[24] We stress that when materials are nonmagnetic with an almost temperature-independent magnetic susceptibility (e.g., Rh metal), no exchange splitting is measured in the $3s$ spectrum. This is different from spin-fluctuations in the paramagnetic phase of ionic systems as in this case with the fast PES probe all Fe atoms would exhibit the same splitting.

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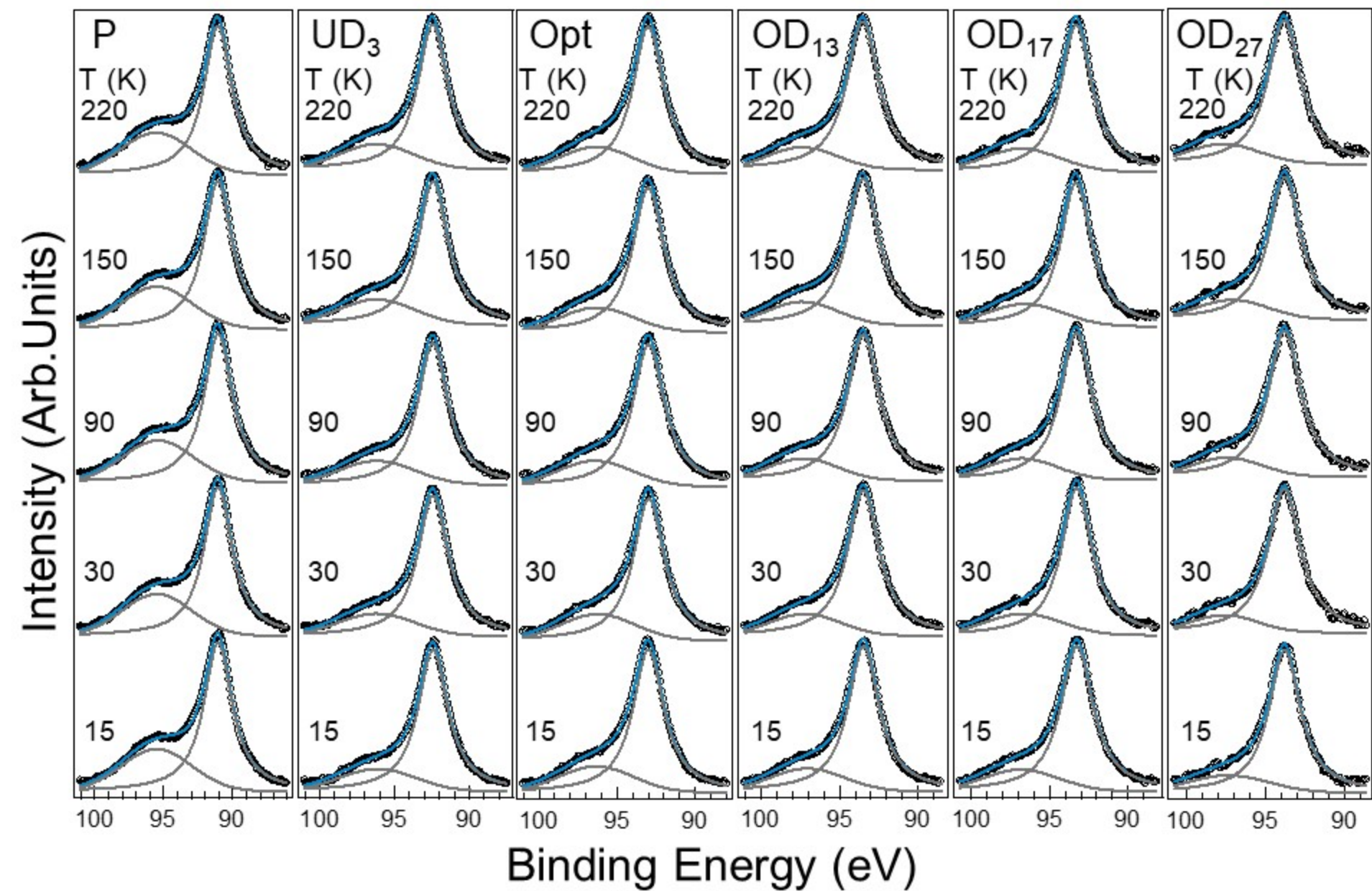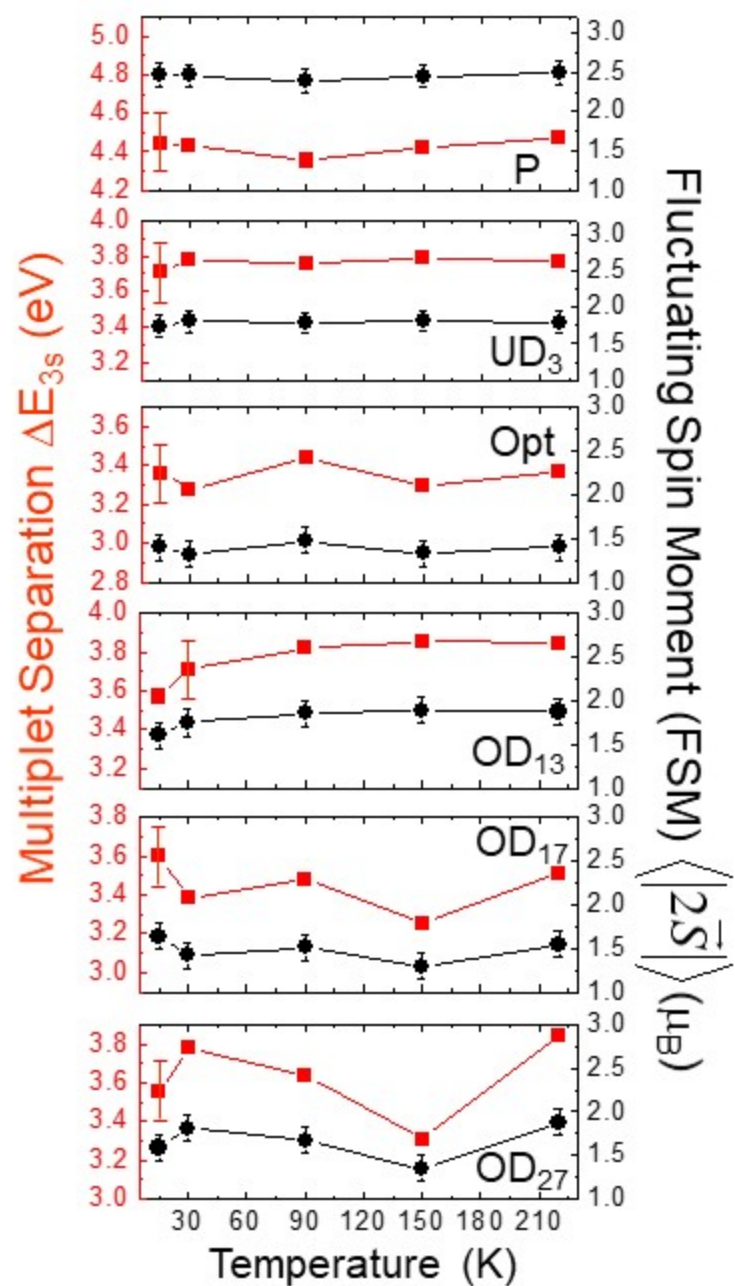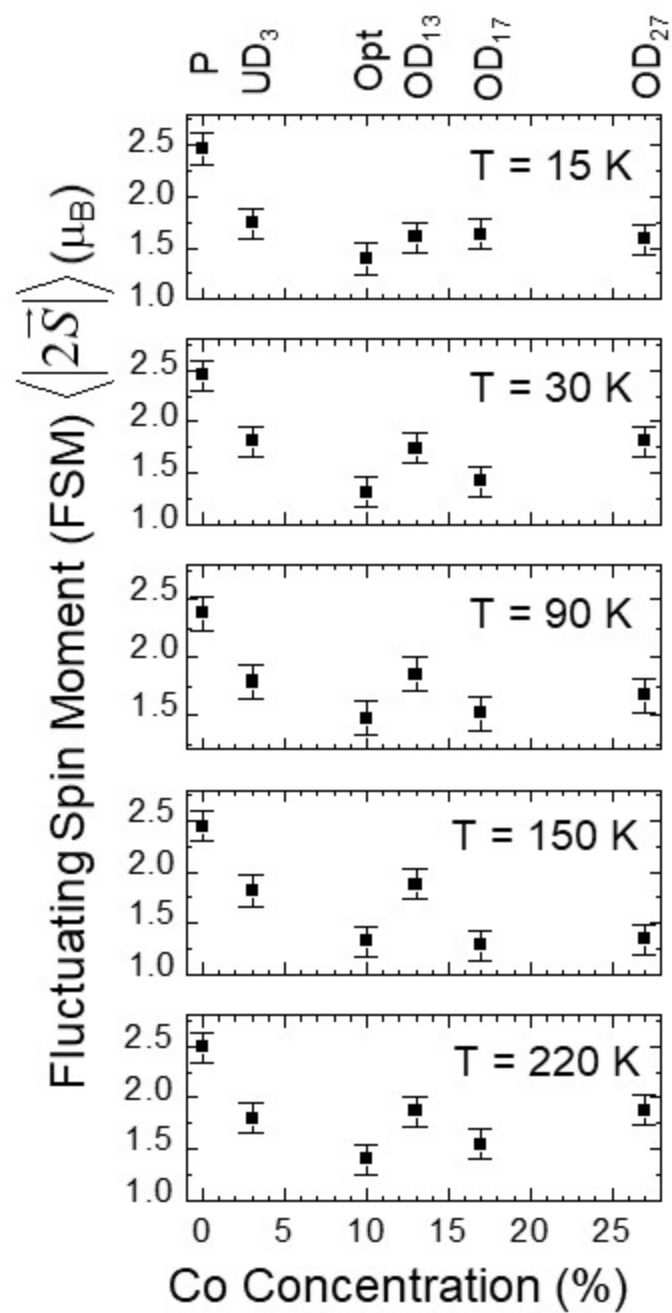Fig. 1

Fig. 2

Fig. 3