Local spin fluctuations in iron-based superconductors: $^{77}$Se and $^{87}$Rb NMR measurements of Tl$_{0.47}$Rb$_{0.33}$Fe$_{1.63}$Se$_2$

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(Dated: January 18, 2013)

We report nuclear magnetic resonance (NMR) studies of the intercalated iron selenide superconductor (Tl,Rb)$_2$Fe$_{2-x}$Se$_2$ ($T_c = 32$ K). Single-crystal measurements up to 480 K on both $^{77}$Se and $^{87}$Rb nuclei show a superconducting phase with no magnetic order. The Knight shifts $K$ and relaxation rates $1/T_1$ increase very strongly with temperature above $T_c$, before flattening at 400 K. The quadratic $T$-dependence and perfect proportionality of both $K$ and $1/T_1$ data demonstrate their origin in paramagnetic moments. A minimal model for this pseudogap-like response is not a missing density of states but two additive contributions from the itinerant electronic and local magnetic components, a framework unifying the $K$ and $1/T_1$ data in many iron-based superconductors.

PACS numbers: 74.70.-b, 76.60.-k

The phenomenon of the pseudogap, an energy scale marking the loss of spin-fluctuation contributions in many physical processes, is ubiquitous in underdoped cuprate superconductors. The origin of the pseudogap and its connection to high-temperature superconductivity have remained controversial questions for over two decades. In the iron pnictide superconductors, the susceptibility and Knight shift in the normal state have been found to increase with temperature. While a pseudogap has been proposed in comparison with cuprates, the evidence is far from conclusive.

The recently discovered intercalated iron selenide superconductors, A$_y$Fe$_{2-x}$Se$_2$, have transition temperatures $T_c > 30$ K. Structural experiments indicate a distinctive $\sqrt{5} \times \sqrt{5}$ ordering pattern of Fe vacancies in the Fe$_4$Se$_5$ layers. Accompanying this structure is an equally distinctive block-spin antiferromagnetic (AFM) order with a very high Néel temperature. By contrast, NMR reveals a superconducting state with only weak low-energy spin fluctuations and no evidence for magnetic order, which is consistent with angle-resolved photoemission spectroscopy. The substantial increases of $K$ and $1/T_1$ reported above $T_c$ in Refs. suggest a strong pseudogap-like effect, and this would set strict constraints on any theoretical models.

In this Letter, we present an extensive $^{77}$Se and $^{87}$Rb NMR investigation of superconducting (Tl,Rb)$_2$Fe$_{2-x}$Se$_2$ single crystals at temperatures up to 480 K. The Knight shifts and relaxation rates on both the $^{77}$Se and $^{87}$Rb sites rise by factors of five to 20 above $T_c$, before leveling off towards 400 K. At low temperatures, our measured response is due to itinerant electrons forming a Fermi liquid. Above $T_c$, we have previously identified a quadratic temperature-dependence of the Knight shift. Here we further demonstrate that the rise of both the Knight shift and the $1/T_1$ follows very accurately a $T^2$ dependence, indicative of fluctuating paramagnetic moments. The leveling off above 400 K suggests that the energy scale of the spin fluctuations is around 35 meV.

Thus our data, whose form is reminiscent of a pseudogap behavior, is best explained by a two-component model. This situation is quite different from cuprates and provides a general basis for interpreting $K$ and $1/T_1$ data in all the Fe superconductors.

The (Tl,Rb)$_2$Fe$_{2-x}$Se$_2$ single crystals were synthesized by the Bridgeman method. Inductively coupled plasma atomic emission spectroscopy measurements give a nominal chemical composition of Tl$_{0.47}$Rb$_{0.33}$Fe$_{1.63}$Se$_2$. Several crystals, all of dimensions 5 × 4 × 1 mm$^3$ and $T_c = 32 \pm 1$ K, were used in our NMR experiments, and all gave consistent results. A specially adapted NMR probe of our own construction was used to access both low and high temperatures. We have performed $^{87}$Rb ($\gamma_m = 13.931$ MHz/T) and $^{77}$Se ($\gamma_m = 8.131$ MHz/T) measurements in a magnetic field of 11.62 T, with the sample placed on a rotator to change the field orientation. The spectral linewidth is approximately 25 kHz for $^{87}$Rb and 20 kHz for $^{77}$Se at $T = 40$ K. The spin-lattice relaxation rate $1/T_1$ is measured by the inversion-recovery method, and a single $T_1$ component is obtained.
Figure 2(a) shows the NMR spectra of the $^{87}$Rb central transition at different temperatures. The central frequency shifts upward gradually with temperature. The spin-spin relaxation rate $1/T_2$ also increases with temperature [Fig. 2(c)], until the NMR spectrum becomes undetectable beyond 480 K, where $T_2$ becomes too short. After correction for $T_2$ effects, the spectral weight is conserved over the full temperature range of our studies [Fig. 2(b)]. For $^{77}$Se, $T_2$ also becomes shorter with increasing temperature (data not shown), and the $^{77}$Se spectrum is not detectable above 420 K.

In Figs. 2(a) and (b), we show $^{87}$K and $^{77}$K in fields applied along the crystalline c axis and in the (ab) plane, and over a very wide range of temperature. The Knight shifts for the two field orientations are nearly identical. The two nuclei also have rather similar temperature-dependences. Focusing first on the region below $T_c$, in general the Knight shift $K = K_x + K_y$ has both chemical ($K_x$) and spin ($K_y$) contributions. $K_x$ is independent of temperature while $K_y$ approaches zero for a singlet superconductor. Singlet superconductivity is therefore demonstrated quite unambiguously by the sharp drop below $T_c$.

For temperatures far below $T_c$, $K(T) \approx 0$ suggests that $K_x$ is very small in the $\mathrm{A}_y\mathrm{Fe}_{2-x}\mathrm{Se}_2$ materials and this contribution will be neglected hereafter.

Turning to the normal-state behavior of $K(T)$, it is almost isotropic and comparable on both $^{77}$Se and $^{87}$Rb nuclei. It increases strongly from $T_c$ to 400 K [Figs. 2(a) and (b)] before flattening out. This form is reminiscent of a pseudogap, where spin fluctuations contributing to $K(T)$ are suppressed below a characteristic energy scale, $\Delta_{pg}$. In the simplest pseudogap scenario, $K(T)$ at low $T$ should contain a thermally activated contribution and $\Delta_{pg}$ can be extracted from the data.

We test for such activated behavior in Fig. 2(a). The expressions $^{87}K(T) = 0.066\% + 0.946\%e^{-500K/T}$ and $^{77}K(T) = 0.1\% + 2.73\%e^{-502K/T}$ provide adequate fits over the full range from $T_c$ to 350 K [inset, Fig. 2(a)], and suggest an effective gap scale around 500 K. However, $K(T)$ levels off around 400 K, and a detailed inspection of the low-$T$ regime in a standard activation plot [Fig. 3(a)] shows clearly that $K(T)$ does not follow this form below 150 K. The fitting contains no evidence for a pseudogap energy scale and the data require an alternative explanation.

In fact an excellent fit to all of the Knight-shift data below 300 K [Figs. 2(a) and (b)], is provided by the function $K(T) = a + bT^2$, where $^{77}K(T) = 0.079\% + 5.978 \times 10^{-6}T^2/K^2$ and $^{87}K(T) = 0.055\% + 2.706 \times 10^{-6}T^2/K^2$. For comparison with the activated scenario, the data and fit are reproduced in Fig. 2(b). Only above 300 K do the measured Knight shifts deviate from the $T^2$ behavior as the data begin to saturate. Even more remarkably, the relaxation rates for both nuclei, shown in Figs. 2(c) and (d) and also analyzed in Fig. 2(b), have precisely the same behavior from $T_c$ to 300 K, with $1/T_1T = 0.136s^{-1}K^{-1} + 2.329 \times 10^{-5}T^2s^{-1}K^{-3}$ and $1/T_2T = 0.014s^{-1}K^{-1} + 3.905 \times 10^{-6}T^2s^{-1}K^{-3}$. The quadratic $T$-dependence of both quantities is completely unambiguous, and we discuss its physical meaning below.

We further analyze our data by comparing $K(T)$ to $(T_1T)^{-1}$ with temperature as the implicit parameter. A system with Fermi-liquid behavior follows the Korringa relation, $(T_1T)^{-1/2} \propto K(T)$.

A linear relation between
**FIG. 4:** (color online) \((T_1T)^{-1/2}\) (left axis) and \((T_1T)^{-1}\) (right) against \(K\) for (a) \(^{87}\text{Rb}\) with \(T_c \leq T \leq 425\) K and (b) \(^{77}\text{Se}\) with \(T_c \leq T \leq 300\) K. Straight lines are guides to the eye.

\(K(T)\), which measures the \(q = 0\) response, and \((T_1T)^{-1}\), which is the \(q\)-integrated response, is the hallmark of relaxation processes dominated by local spin fluctuations. It is clear from Figs. 4(a) and (b) that the Korringa relation is not followed over any of the temperature range, whereas good linear proportionality is obtained between \(K(T)\) and \((T_1T)^{-1}\). We conclude that spin fluctuations are the predominant relaxation mechanism above \(T_c\), and that these are very local in nature as there is no significant contribution from particular wave vectors \(\mathbf{Q} \neq 0\).

We stress here that the fitting lines in Figs. 4(a) and (b) do not pass through the origin. Both \(K(T)\) and \(1/T_1T\), for both nuclei, approach constant values as \(T \to T_c\). Such constant terms above \(T_c\) usually indicate an additional Fermi-liquid contribution from itinerant electrons, which is lost as the system becomes superconducting below \(T_c\) (Fig. 2). The Fermi-liquid contribution may be extracted by writing \(K(T) = K_0 + f(T)\) and \(1/T_1T = (1/T_1T)_0 + f'(T)\), where the \(T\)-dependence, contained only in \(f(T)\) and \(f'(T)\), is quadratic. This explicit separation of itinerant-electron and spin-fluctuation contributions is completed by identifying the two ratios \((1/T_1T)_0/K_0\) and \(f'(T)/f(T)\), whose respective values are 34 s\(^{-1}\)K\(^{-1}\) and 170 s\(^{-1}\)K\(^{-1}\) for \(^{87}\text{Rb}\), and 190 s\(^{-1}\)K\(^{-1}\) and 350 s\(^{-1}\)K\(^{-1}\) for \(^{77}\text{Se}\).

We conclude the analysis of our data with two further comments on the Knight shift. First, the anisotropy is very small, with \(^{77}K_{ab}/^{77}K_c \approx 1.1\) and \(^{87}K_{ab}/^{87}K_c \approx 1.0\) at 300 K (Fig. 2). Second, the ratio \(^{87}K/^{77}K \approx 0.4\) at 300 K indicates that the amplitudes of the hyperfine fields, which are produced by the Fe moments, are quite similar at the in-plane Se site and the interlayer Rb site. These results suggest a strong interlayer magnetic coupling in the intercalated iron selenides. In the iron pnictides, the hyperfine fields are usually very much smaller at the interlayer nuclei than at the \(^{75}\text{As}\) site \(^{34,35}\).

Before discussing the two-component interpretation of our NMR measurements, we discuss the necessity for a two-phase scenario in the \(A_y\Fe_{2-x}\Se_2\) materials. The block-AFM state of the \(\sqrt{5} \times \sqrt{5}\) structure has a high \(T_N \approx 550\) K and a large magnetic moment of order \(3\mu_B\) per Fe site. These neutron-diffraction results \(^{18,19}\) have been verified by bulk magnetization \(^{20}\) muon spin resonance (\(\mu\text{SR}\)) \(^{21}\), Mössbauer \(^{22}\) two-magnon Raman \(^{23}\) and inelastic neutron scattering measurements \(^{24}\). However, the superconducting phase observed by NMR is clearly paramagnetic, because the large line-splitting of the \(^{77}\text{Se}\) spectra, expected for a strongly AFM state, is completely absent. Further, the Knight shift would not be nearly isotropic in the presence of AFM order.

We are forced to conclude that the electronic matter in \(A_y\Fe_{2-x}\Se_2\) is a two-phase system. The AFM phase is thought from \(\mu\text{SR}\) and neutron diffraction experiments to constitute at least 90% of this system. The paramagnetic, metallic phase we observe, which makes up the remainder, may be a consequence of regions within the single crystals with different Fe vacancy content or vacancy disorder. The paramagnetic phase is manifestly superconducting. Whether the AFM phase is an insulator while the paramagnetic phase percolates throughout the system to give the observed bulk superconducting properties, or is a metal hosting a microscopic coexistence of magnetism and superconductivity, remains an open question that NMR cannot address.

Returning now to the NMR response of the paramagnetic phase, the minimal model describing our experimental data is simply one with two additive components. One is the metallic behavior of the itinerant electrons, which become superconducting below \(T_c\) and appear above \(T_c\) as a \(T\)-independent constant. The origin of the quadratic \(T\)-dependence above \(T_c\) lies in local fluctuations of the paramagnetic Fe moments, which may be as large as the \(3\mu_B\) observed in the AFM phase. These moments have only short-range order, with local AFM fluctuations, and while the system is close to the long-range order of the neighboring magnetic phase, this is prevented by some combination of non-stoichiometry, vacancy disorder, and the effects of the itinerant electrons.

In studies of quantum AFMs, paramagnetic spins in a critical regime with no spin gap give a linear contribution to the susceptibility in two dimensions (2D) and a quadratic \(T\)-dependence in 3D \(^{26}\). Similar considerations have been applied in pnictide superconductors to discuss the linear susceptibility in a 2D model \(^{27}\) for 1111 and 122 systems. The large values of \(^{87}K(T)\) we measure are a definite indication of strong interlayer magnetic coupling and 3D nature in the \(A_y\Fe_{2-x}\Se_2\) materials, and hence are fully consistent with a quadratic spin-fluctuation contribution. The temperature at which our data begin to turn over, \(T \sim 400\) K, also agrees well with the predominant energy scale for local spin-exchange processes, \(|S|J| = 36\) meV, deduced in Ref. \(^{38}\); this further strengthens the evidence in favor of fluctuating local moments rather than electronic processes.

While it may be possible to conceive of a pseudo-gap model with an exact constant contribution, exactly...
quadratic $T$-dependence, exact proportionality of $K$ and $1/T_1 T$ over the entire temperature range above $T_c$, and the observed dramatic increases in these quantities, this would require very careful fine-tuning. Thus we find a two-component scenario to be much more likely, and it is certainly the minimal model for our results. Its foundation lies in the fact that Fe has active conduction and valence bands, the former providing itinerant electrons and the latter forming effective local moments $^{32,33}$ A two-component model has also been invoked to explain EPR and NMR data in FeSe $^{11}$ and NMR data in 111 materials $^{45,46}$ This situation is not at all similar to the superconducting cuprates, where the NMR response is attributed to a single electronic component (in one active Hubbard band) experiencing spin-fluctuation correlations that reduce its spin contribution. In Fe superconductors, no such correlation effects are required.

We extend these considerations to the NMR data obtained for other iron-based superconductors. Our results are almost identical to those for $K_y$Fe$_2-x$Se$_2$ $^{22,23}$ while the binary iron selenides also show a similarly substantial $T^2$-type increase up to 300 K on top of a constant contribution $^{22,23}$ shown in Fig. 3(b) using $^{77}$K data adapted from Ref. $^{31}$. This indicates universal behavior in the FeSe planes of the chalcogenides. In the three known iron pnictide superconductors, weak increases of $K(T)$ above $T_c$ have also been interpreted as pseudogap behavior. In both the 1111 $^{11,15}$ and 111 $^{45,46}$ systems, the $T$-dependent part of $K$ and $1/T_1 T$ is small and almost linear, suggesting only a weak contribution from quasi-2D spin fluctuations. The 122 systems deviate from this paradigm only at low temperatures $^{18}$ while $K$ has a small spin-fluctuation part with a possibly quadratic (3D) $T$-dependence, $1/T_1 T$ shows an increase towards low $T$ for most dopings, indicating a role for magnetic modes with $Q \neq 0$.

Thus the two-component framework forms a basis for the normal-state NMR response of all the Fe superconductors. This general result provides important guidance to both experimental and theoretical understanding of these materials far beyond NMR measurements. The importance of local spin fluctuations and the lack of relevance of particular magnetic modes, despite the proximity to magnetic phases, are essential clues to the mechanism for superconductivity. The clear presence of both Fermi-liquid and local-moment behavior reflects the generic property of the Fe superconductors that both conduction and valence electrons play a crucial role.

In summary, our NMR measurements on the intercalated iron selenide superconductor (Tl,Rb)$_x$Fe$_2-x$Se$_2$ show a large increase of the isotropic Knight shift and the spin-lattice relaxation rate with temperature above $T_c$. The temperature-dependence of this contribution is quadratic. We deduce that pseudogap-like behavior in the paramagnetic, metallic phase is the consequence of two separate contributions, one from itinerant electrons, which become superconducting below $T_c$, and one from local 3D spin fluctuations of disordered Fe moments, which become dominant above $T_c$. Such a two-component model provides a framework for understanding the $K$ and $1/T_1 T$ data in all Fe superconductors.

The authors acknowledge W. Bao, S. E. Brown, J. Hu, T. Li, Z. Y. Lu, Y. Su, X. Q. Wang, T. Xiang, D.-X. Yao, G. Zhang, Q. M. Zhang, and X. J. Zhou for helpful discussions. This work was supported by the NSFC under Grant Nos. 10974254, 11074304, and 10874244, and the National Basic Research Program of China under Grant Nos. 2010CB923000 and 2011CBA00112. W.Y. is supported by the “New Century Program for Excellent Talent in Universities” of the Chinese MoE.

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