Magnetic field dependence of spin-lattice relaxation in the s± state of Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$

Sangwon Oh$^1$, A. M. Mounce$^1$, W. P. Halperin$^1$, C. L. Zhang$^2$, Pengcheng Dai$^2$, A. P. Reyes$^3$, P. L. Kuhns$^3$

$^1$Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208, USA
$^2$Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA
$^3$National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA
(Dated: Version May 1, 2012)

The spatially averaged density of states, $\langle N(0) \rangle$, of an unconventional $d$-wave superconductor is magnetic field dependent, proportional to $H^{1/2}$, owing to the Doppler shift of quasiparticle excitations in a background of vortex supercurrents. This phenomenon, called the Volovik effect, has been predicted to exist for a sign changing $s \pm$ state although it is absent in a single band $s$-wave superconductor. Consequently, we expect there to be Doppler contributions to the NMR spin-lattice relaxation rate, $1/T_1 \propto \langle N(0)^2 \rangle$, for an $s \pm$ state which will depend on magnetic field.

We have measured the $^{75}$As $1/T_1$ in a high-quality, single crystal of Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ over a wide range of field up to 28 T. Our spatially resolved measurements show that indeed there are Doppler contributions to $1/T_1$ which increase closer to the vortex core, with a spatial average proportional to $H^2$, inconsistent with recent theory.\footnote{In this Letter, we report $^{75}$As NMR measurements in single crystals of Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ covering a wide range of magnetic fields.}

We performed our $^{75}$As NMR measurements at Northwestern University and the National High Magnetic Field Laboratory, from 4 K to room temperature with external magnetic field from 6.4 to 28 T. The fields were parallel to the $c$-axis of the single crystals, Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ (BaK122) that had a zero-field $T_c = 38$ K and were grown at the University of Tennessee by the self-flux method.\footnote{To increase signal intensity in the superconducting state, the crystals were cleaved to dimensions of $3 \times 3 \times 0.1$ mm$^3$ and total mass of 17 mg. Typically, spin echo sequences $(\pi/2 - \pi)$ were used to obtain the spectrum, Knight shift, and $1/T_1$ for the central transition (-1/2 ↔ 1/2) with a $\pi$-pulse $\approx 7$ µsec. The spin-lattice relaxation was measured with the full recovery method (28 to 300 K) and progressive saturation techniques (4 to 26 K) the latter being more accurate for very long relaxation times at low temperatures. The average rate was measured with the $\pi$-pulse centered on the spectrum. Frequency-resolved spin-lattice relaxation was also measured by dividing the spectrum into many small frequency windows and the relaxation was determined separately in each window. Knight shift measurements were performed with a frequency sweep method.}

Early experiments on optimally, hole-doped, single crystals of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$\footnote{Early experiments on optimally, hole-doped, single crystals of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ grown with tin flux did not detect any signal below 20 K due to linewidth broadening from paramagnetic impurities on the As sites at a level of $\approx 1%$. However, there have been substantial improvements in lowering the impurity concentration using the self-flux method.} grown with tin flux did not detect any signal below 20 K due to linewidth broadening from paramagnetic impurities on the As sites at a level of $\approx 1%$. However, there have been substantial improvements in lowering the impurity concentration using the self-flux method. The frequency-swept $^{75}$As

PACS numbers:
NMR spectra of our crystals in 13 T with \( H \parallel c \)-axis, are shown in Fig. 1. The \( T_c \) in \( H = 13 \) T is 32 K, and a shift of the spectra can be easily seen. This decrease of the Knight shift indicates spin-singlet pairing in the superconducting state. On cooling, the linewidth slowly broadens from 60 kHz at \( T = 300 \) K to 70 kHz at \( T_c \). Below \( T_c \) the linewidth increases up to 110 kHz near 20 K, and then it decreases to 80 kHz at 4 K, and is independent of magnetic field from 6.4 to 16.5 T, to within 10%. The weak dependence of the linewidth on magnetic field and temperature in the normal state indicates that few magnetic impurities are present, comparable to the cleanest cuprate crystals such as Bi\(_2\)SrCa\(_2\)Cu\(_2\)O\(_{8+\delta}\) (Bi2212). This point is also consistent with the similar results we find from our comparison of the zero field extrapolations of \( 1/T_1 \) with those of clean Bi2212 crystals which we discuss later. The Knight shift, \( K = K_s + K_{\text{orb}} \), was determined from the first moment of the NMR spectrum where \( K_s \) and \( K_{\text{orb}} \) are the spin and orbital parts of the shift, respectively. The orbital part is temperature and field independent, consequently the temperature dependence of the shift in Fig. 2 can be associated with \( K_s \), decreasing below \( T_c \) on cooling. The solid curve in the figure is the temperature dependence of \( K_s \) that we describe with a phenomenological model for the density of states, Eq. 1 based on the parameters obtained from \( 1/T_1 \) measurements.

The behavior of the spin-lattice relaxation in the superconducting state is the main focus of our present work where we measure the temperature and magnetic field dependence for \( H = 6.4, 10.8, 14, 16.5, 27 \) and \( 28 \) T, parallel to the \( c \)-axis of the crystals. The rates were measured with the spectrometer frequency set at the peaks of the spectra. A coherence peak below \( T_c \) was not observed, and the suppression of \( T_c \) by the magnetic field was minimal, from \( T = 32 \) to 30 K when the external field was increased from 6.4 to 27 T. In low magnetic fields, \( i.e. \) 6.4 and 10.8 T, the temperature dependence of \( 1/T_1 \) could be approximately described as \( T^3 \) at intermediate temperature, as has often been reported elsewhere. But in higher fields, 14, 16.5, 27 T, below \( T = 10 \) K, we find \( 1/T_1 \propto T \), indicating a constant average density of states at zero energy, \( \langle N(0) \rangle \). Recently Li et al. observed an exponential temperature dependence of the rate in a magnetic field of \( H = 7.5 \) T consistent with the presence of a full gap. A comparison of our data with that of Li et al., shows that they are identical except at our lowest temperature, \( T = 4 \) K, where our higher value of \( 1/T_1 \) might be understood as the effect of residual impurities in our crystal obscuring exponential behavior. Increasing the magnetic field we find that the spin-lattice relaxation at 4 K increases systematically indicating the existence of a field dependent density of states at the Fermi surface. This observation is a characteristic signature of a Volovik effect.

We use a phenomenological model to fit \( 1/T_1 \) in various magnetic fields. We express the thermal and spatial average over the density of states at the Fermi surface as,

\[
\langle N(0) \rangle = a(H) + b_0 e^{-\Delta_1/k_B T} + c_0 e^{-\Delta_2/k_B T}
\]  

where \( a(H) = a_0 + a_1 H + ... \) and \( a_0 \) represents possible contributions from non-magnetic impurities. The two gaps, \( \Delta_1 \) and \( \Delta_2 \), appear in exponential terms with relative weights, \( b_0 \) and \( c_0 \), as might be expected for the low temperature limit. Since \( 1/T_1 \propto \langle N(0) \rangle^2 \), our model...
for $1/T_1 T$ becomes,

$$1/T_1 T \propto [a(H) + b_0 e^{-\Delta_1/k_B T} + c_0 e^{-\Delta_2/k_B T}]^2. \quad (2)$$

At low temperatures the two exponential terms are of little importance and the rate is determined by $a(H)$. Our numerical analysis provides fits for all of the parameters of the model. Below $H = 16.5$ T, we take them to be magnetic field independent. However, at this and higher magnetic fields we find that the relative weight of the exponential term from the smaller gap, $b_0$, must be reduced compared to the larger gap weight, $c_0$, in order to fairly represent the data. As stated previously, these gap parameters are not important in the low temperature limit where we seek to describe the field dependence of the relaxation rate and so we do not ascribe specific importance to this additional field dependence other than it allows us to represent the high temperature behavior in each field. Nonetheless, we point out that our results for the temperature dependence at low magnetic field are identical to those from Li et al.\cite{Li2012} for clean crystals, except for the lowest temperature point at 4 K.

Our analysis in each field is shown in Fig. 3(a)-(e), where $\Delta_1$ and $\Delta_2$ are $2.1 \pm 0.2$ meV and $12.1 \pm 1.4$ meV respectively. The sizes of the gaps correspond well to the sizes of the 3D superconducting gap function from ARPES measurements, 2.07 meV and 12.3 meV. The ratio of the coefficients, $b_0$ and $c_0$, decreases at $H = 16.5$ and 27 T, indicating a possible suppression of the smaller superconducting gap, $\Delta_1$, by the external magnetic field. The low temperature magnetic field dependence of $1/T_1 T$ is given by $a(H)$ shown in Fig. 3(f). The $H^2$ behavior might be associated with Doppler shifted quasiparticles, although the field dependence is different from that predicted by theory.\cite{Dynes1982} It should be noted that the electronic Zeeman interaction also contributes to the quasiparticle energy giving a $H^2$ dependence to $1/T_1 T$.\cite{Dynes1982} In Fig. 4(a)-(f) we show the field dependence of $1/T_1 T$ for $^{17}$O NMR from YBa$_2$Cu$_3$O$_{7+\delta}$ (Y123) aligned powders\cite{Zhou2013} and Bi2212 crystals\cite{Yang2013} which has been attributed to this Zeeman term. From comparison with these compounds, allowing for the 27% larger gyromagnetic ratio of arsenic compared to oxygen, it is reasonable to conclude that our BaK122 crystal does not have significantly more impurity scattering than these high quality cuprate materials.
at $T = 40$ K is independent of magnetic field for $H \leq 16.5$ T to within 10%, we do not associate the field dependence of the rate with magnetic impurities. However, this possibility can be investigated further by measurement of the frequency-resolved spin-lattice rate which we describe next.

For unconventional superconductors $1/T_1$ can depend on the position of the probe nucleus relative to the vortex core.\textsuperscript{19,21} The increase in the supercurrent momentum, $p_v$, approaching the core leads to a corresponding increase in the Doppler shift of the energy of quasiparticle excitations, $v_F \cdot p_v$, where $v_F$ is Fermi velocity. The vortex core, having the highest local magnetic field, corresponds to the largest frequency in the NMR spectrum. We have looked for evidence of this spatial dependence of $1/T_1$ through frequency-resolved, \textit{i.e.} spatially resolved, measurements performed across the spectrum, as shown in Fig. 5.

In the normal state (40 K) we find a flat $1/T_1$ distribution throughout the spectrum as expected in the absence of Doppler terms or magnetic impurity contributions to the rate. In the superconducting state, there is an increase of $1/T_1$ with frequency, developing markedly at $T = 26$ K with more than an order of magnitude variation across the spectrum.

![Graphs showing $1/T_1$ vs frequency at different temperatures and fields](image)

FIG. 5: Spin-lattice relaxation rate across spectrum in the normal state (a) and superconducting states (b), (c), (d) in 16.5 T, with $H || c$-axis. In the normal state, at 40 K, there is no significant frequency dependence in $1/T_1$. However, the rate becomes dependent on frequency as the sample is cooled deep into the superconducting state.

We note that the linewidth, $\sim 80$ kHz at 4 K in $H = 16.5$ T is somewhat broader than our calculation from Ginzburg-Landau theory using Brandt’s algorithm\textsuperscript{22} for a perfect vortex lattice, $\sim 23$ kHz. However, even in a somewhat disordered vortex structure, the high field portion of the spectrum can be associated with nuclei in the vortex core. This is the case for the distribution in $1/T_1$ observed in Y123, which was attributed to the Doppler shift\textsuperscript{23} of quasiparticle energy from vortex supercurrents. Our frequency-resolved measurements of $1/T_1$ in BaK122, Fig. 5, show the existence of a spatially inhomogeneous distribution which onsets with superconductivity. We ascribe this to the vortex state for which the most likely explanation is a Volovik effect. Another explanation was suggested some years ago to explain observations in superconducting vanadium compounds.\textsuperscript{23,24} There it was argued that spin-diffusion from relaxation sources in the vortex core might produce a spatially inhomogeneous distribution of $1/T_1$. Later measurements and theoretical work by Genack and Redfield\textsuperscript{23,24} showed that this suggestion was incorrect, and that spin diffusion is quenched on very short time scales owing to depletion of the dipole energy reservoir, an effect even further suppressed with increasing field. We measured the spin lattice relaxation rates in higher fields, 24 T and 28 T, as shown in Fig. 6. An inhomogeneous spin-lattice relaxation rate distribution was found similar to that of $H = 16.5$ T, Fig. 5 and rules out spin diffusion as a possible mechanism.\textsuperscript{23,24}

With reports from experiments in cuprates a decade ago,\textsuperscript{19,27} this mechanism was studied theoretically by Wortis\textsuperscript{28} who came to the same conclusion. A more detailed discussion has been provided by Mounce \textit{et al.}\textsuperscript{29} We point out that in the recent theory\textsuperscript{24} of the Volovik effect in $s\pm$ superconductors the combined effects of the Zeeman interaction and vortex supercurrents have not been taken into account. Their importance was indicated in the work of Mitrović \textit{et al.} on YBa$_2$Cu$_3$O$_7$\textsuperscript{25} and might be an important component missing from the theory. We conclude that our observations are most likely a consequence of vortex supercurrents but for which there is not yet a satisfactory theoretical explanation.

In summary, we have studied the 75As Knight shift...
and spin-lattice relaxation rate in slightly underdoped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ crystals in the superconducting mixed state. We found that $1/T_1 T$ approaches a constant at low temperatures in high magnetic field and is proportional to the square of the field. Although this is inconsistent with a theory for the Volovik effect our results can be accounted for by a phenomenological model which is based on $s\pm$ symmetry with two isotropic gaps, and non-magnetic impurities. The distribution of $1/T_1$ across the spectrum resembles that observed in a vortex solid of an unconventional superconductor associated with spatially resolved Doppler contributions to the quasiparticle excitation spectrum.

We thank Y. Bang, G.E. Volovik, P.J. Hirschfeld, and J.A. Sauls for helpful discussions. Research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Awards DE-FG02-05ER46248 (Northwestern University) and No. DE-FG02-05ER46202 (the University of Tennessee). Work at high magnetic field was performed at the National High Magnetic Field Laboratory supported by the National Science Foundation and the State of Florida.

1. G. E. Volovik, J. Phys. C. 21, L221 (1988).
2. G. E. Volovik, JETP Lett. 58, 469 (1993).
3. Y. Bang, Phys. Rev. Lett. 104, 217001 (2010).
4. Y. Bang (2011), arXiv.org:1112.0142v2.
5. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
6. Y. Nakai, T. Iye, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibatauchi, Y. Matsuda, and T. Terashima, Phys. Rev. B 81, 020503 (2010).
7. F. L. Ning, K. Ahilan, T. Imai, A. S. Sefat, M. A. McGuire, B. C. Sales, D. Mandrus, P. Cheng, B. Shen, and H.-H. Wen, Phys. Rev. Lett. 104, 037001 (2010).
8. H. Fukazawa, Y. Yamada, K. Kondo, T. Saito, Y. Kohori, K. Kuga, Y. Matsumoto, S. Nakatsuj, H. Kito, P. M. Shirage, et al., J. Phys. Soc. Jpn. 78, 083712 (2009).
9. M. Yashima, H. Nishimura, H. Mukuda, Y. Kitaoka, K. Miyazawa, P. M. Shirage, K. Kihou, H. Kito, H. Eisaki, and A. Iyo, J. Phys. Soc. Jpn. 78, 103702 (2009).
10. Z. Li, D. L. Sun, C. T. Lin, Y. H. Su, J. P. Hu, and G.-q. Zheng, Phys. Rev. B 83, 140506 (2011).
11. H.-J. Grafe, D. Paar, G. Lang, N. J. Curro, G. Behr, J. Werner, J. Hamann-Borrero, C. Hess, N. Leps, R. Klinger, et al., Phys. Rev. Lett. 101, 047003 (2008).
12. S. K. Yip and J. A. Sauls, Phys. Rev. Lett. 69, 2264 (1992).
13. C. Zhang, M. Wang, H. Luo, M. Wang, M. Liu, J. Zhao, D. L. Abernathy, T. A. Maier, K. Marty, M. D. Lumsden, et al., Scientific Reports 1, 115 (2011).
14. V. F. Mitrović, E. E. Sigmund, and W. P. Halperin, Phys. Rev. B. 64, 024520 (2001).
15. B. Chen, W. P. Halperin, P. Guptasarma, D. G. Hinks, V. F. Mitrović, A. P. Reyes, and P. L. Kuhns, Nature Physics 3, 239 (2007).
16. S. Oh, A. M. Mounce, S. Mukhopadhyay, W. P. Halperin, A. B. Vorontsov, S. L. Bud’ko, P. C. Canfield, Y. Fukuda, A. P. Reyes, and P. L. Kuhns, Phys. Rev. B. 83, 214501 (2011).
17. S. Mukhopadhyay, S. Oh, A. M. Mounce, M. Lee, W. P. Halperin, N. Ni, S. L. Bud’ko, P. C. Canfield, A. P. Reyes, and P. L. Kuhns, New J. Phys. 11, 055002 (2009).
18. Y.-M. Xu, Y.-B. Huang, X.-Y. Cui, E. Razzoli, M. Radovic, M. Shi, G.-F. Chen, P. Zheng, N.-L. Wang, C.-L. Zhang, et al., Nature Physics 7, 198 (2011).
19. V. F. Mitrović, E. E. Sigmund, E. Eschrig, H. N. Berman, W. P. Halperin, A. P. Reyes, P. Kuhns, and W. G. Moulton, Nature 413, 501 (2001).
20. A. M. Mounce, S. Oh, S. Mukhopadhyay, W. P. Halperin, A. P. Reyes, P. L. Kuhns, K. Fujita, M. Ishikado, and S. Uchida, Phys. Rev. Lett. 106, 057003 (2011).
21. M. Takigawa, M. Ichioka, and K. Machida, Phys. Rev. Lett. 83, 3057 (1999).
22. E. H. Brandt, Phys. Rev. Lett. 78, 2208 (1997).
23. B. Silbernagel, M. Weger, and J. Wernick, Phys. Rev. Lett. 17, 384 (1966).
24. B. G. Silbernagel, M. Weger, W. G. Clark, and J. H. Wernick, Phys. Rev. 153, 535 (1967).
25. A. Genack and A. Redfield, Phys. Rev. Lett. 31, 1204 (1973).
26. A. Genack and A. Redfield, Phys. Rev. B 12, 78 (1975).
27. N. J. Curro, C. Milling, J. Haase, and C. P. Slichter, Phys. Rev. B 62, 3473 (2000).
28. R. Wortis, Ph.D. thesis, University of Illinois Champaign Urbana (1998); R. Wortis, A. J. Berlinsky, and C. Kallin, Phys. Rev. B 61, 12342 (2000).
29. A. Mounce, S. Oh, and W. Halperin, Front. Phys. 6, 450 (2011).