Neutron scattering study of the oxypnictide superconductor LaO$_{0.87}$F$_{0.13}$FeAs

Y. Qiu, M. Kofu, Wei Bao, S.-H. Lee, Q. Huang, J. R. D. Copley, J. W. Lynn, T. Wu, G. Wu, and X. H. Chen

$^1$NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899
$^2$Dept. of Materials Science and Engineering, University of Maryland, College Park, MD 20742
$^3$Department of Physics, University of Virginia, Charlottesville, VA 22904
$^4$Los Alamos National Laboratory, Los Alamos, NM 87545
$^5$Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

(Dated: May 7, 2008)

The newly discovered superconductor LaO$_{0.87}$F$_{0.13}$FeAs ($T_C \approx 26$ K) was investigated using the neutron scattering technique. No spin-density-wave (SDW) order was observed in the normal state nor in the superconducting state, both with and without an applied magnetic field of 9 T, consistent with the proposal that SDW and superconductivity are competing in the laminar materials. While our inelastic measurements offer no constraints on the spin dynamic response from $d$-wave pairing, an upper limit for the magnetic resonance peak predicted from an extended $s$-wave pairing mechanism is provided. Our measurements also support the energy scale of the calculated phonon spectrum which is used in electron-phonon coupling theory, and fails to produce the high observed $T_C$.

A new family of superconductors has been discovered in oxypnictide La(O,F)FeP ($T_C \approx 4$ K) $^1$, LaO NiP ($T_C \approx 3$ K) $^2$, and La(O,F)FeAs ($T_C \approx 26$ K) $^3$. Enormous excitement has been generated since the discovery at $3 K$ $^2$, and La(O,F)FeAs at $26 K$ $^3$. The parent compounds are superconductors except in some cuprates.

The parent compounds $Ln$OFeAs ($Ln$=La$^8$, Sm$^{11}$, Ce$^5$, Nd, Gd$^8$) are not superconductors. Instead, a new family of superconductors has been discovered in oxypnictide La(O,F)FeP ($T_C \approx 4$ K) $^1$, LaONiP ($T_C \approx 3$ K) $^2$, and La(O,F)FeAs ($T_C \approx 26$ K) $^3$. Enormous excitement has been generated since the discovery at $3 K$ $^2$, and La(O,F)FeAs at $26 K$ $^3$. The parent compounds are superconductors except in some cuprates.

The parent compounds $Ln$OFeAs ($Ln$=La$^8$, Sm$^{11}$, Ce$^5$, Nd, Gd$^8$) are not superconductors. Instead, a new family of superconductors has been discovered in oxypnictide La(O,F)FeP ($T_C \approx 4$ K) $^1$, LaONiP ($T_C \approx 3$ K) $^2$, and La(O,F)FeAs ($T_C \approx 26$ K) $^3$. Enormous excitement has been generated since the discovery at $3 K$ $^2$, and La(O,F)FeAs at $26 K$ $^3$. The parent compounds are superconductors except in some cuprates.

The parent compounds $Ln$OFeAs ($Ln$=La$^8$, Sm$^{11}$, Ce$^5$, Nd, Gd$^8$) are not superconductors. Instead, a new family of superconductors has been discovered in oxypnictide La(O,F)FeP ($T_C \approx 4$ K) $^1$, LaONiP ($T_C \approx 3$ K) $^2$, and La(O,F)FeAs ($T_C \approx 26$ K) $^3$. Enormous excitement has been generated since the discovery at $3 K$ $^2$, and La(O,F)FeAs at $26 K$ $^3$. The parent compounds are superconductors except in some cuprates.

The parent compounds $Ln$OFeAs ($Ln$=La$^8$, Sm$^{11}$, Ce$^5$, Nd, Gd$^8$) are not superconductors. Instead, a new family of superconductors has been discovered in oxypnictide La(O,F)FeP ($T_C \approx 4$ K) $^1$, LaONiP ($T_C \approx 3$ K) $^2$, and La(O,F)FeAs ($T_C \approx 26$ K) $^3$. Enormous excitement has been generated since the discovery at $3 K$ $^2$, and La(O,F)FeAs at $26 K$ $^3$. The parent compounds are superconductors except in some cuprates.

The parent compounds $Ln$OFeAs ($Ln$=La$^8$, Sm$^{11}$, Ce$^5$, Nd, Gd$^8$) are not superconductors. Instead, a new family of superconductors has been discovered in oxypnictide La(O,F)FeP ($T_C \approx 4$ K) $^1$, LaONiP ($T_C \approx 3$ K) $^2$, and La(O,F)FeAs ($T_C \approx 26$ K) $^3$. Enormous excitement has been generated since the discovery at $3 K$ $^2$, and La(O,F)FeAs at $26 K$ $^3$. The parent compounds are superconductors except in some cuprates.
For superconducting samples LaO$_{1.1}$% of the intensity of the structural (002) peak[13]. The strongest magnetic Bragg peak (1/2,1/2,3/2) is only explained by an associated structure transition[34].

Magnetic moment $M = 0.36(5)\mu_B$ per Fe at 8 K[13] can be explained by an associated structure transition[34]. The strongest magnetic Bragg peak (1/2,1/2,3/2) is only 1.1% of the intensity of the structural (002) peak[13]. For superconducting samples LaO$_{0.87}$Fe$_{0.13}$FeAs and LaO$_{0.89}$Fe$_{0.11}$FeAs, magnetic peaks of the SDW order are not observed above measurement statistics level of about 0.5% of the (002) peak at 8 K[13] and 70 K[14], respectively. Neither does our superconducting sample LaO$_{0.87}$Fe$_{0.13}$FeAs show any detectable SDW order down to 1.6 K in the superconducting state (Fig. 1), nor at 30 K in the normal state (Fig. 2). Applying a magnetic field of 9 T also does not induce any magnetic peak stronger than 0.5% of the (002) exists in the spectra.

Neither does our superconducting sample LaO$_{0.87}$Fe$_{0.13}$FeAs show any detectable SDW order down to 1.6 K in the superconducting state (Fig. 1), nor at 30 K in the normal state (Fig. 2). Applying a magnetic field of 9 T also does not induce any magnetic peak stronger than 0.5% of the (002) Bragg peak. These results support the proposal that the SDW and superconducting order parameters are competing for itinerant electrons and holes on the Fermi surface[12, 19], and do not favor the theory of coexistence of antiferromagnetism with superconductivity in La(O,F)FeAs.

Conventional superconductivity is mediated by phonons, and the phonon spectrum has been calculated for La(O,F)FeAs[15, 21]. It has been used to calculate the electron-phonon coupling, and the $T_C$ from this mechanism is much lower than the observed value[10, 21]. To validate the theoretical calculations, we have measured inelastic neutron scattering from phonons in LaO$_{0.87}$Fe$_{0.13}$FeAs. For polycrystalline samples, the intensity is given by

$$I(Q,\omega) = \sum_i \frac{\sigma_i}{2m_i} \exp(-2W_i) \frac{D_i(\omega)}{\omega} [n(\omega, T) + 1],$$

where $\sigma_i$ and $m_i$ are the neutron scattering cross section and atomic mass of the $i$th atom (La, O, F, Fe, As), $n(\omega, T)$ is the Bose factor, $W_i$ the Debye-Waller factor[33]. The weighted phonon density of states (PDOS) $D(\omega) = \sum_i D_i(\omega)$ in Eq. (1) differs from the bare PDOS calculated in[15, 21] by a factor of the squared modulus of phonon eigenvectors. The measured neutron scattering intensity $I(Q,\omega)$ is further weighted by $\sigma_i/m_i$ of different atoms. But the peak positions in the measured and bare PDOS usually remain the same[35].

In the top frame of figure 3, the measured $I(\omega) = \int dQ I(Q,\omega)$ at 1.6 and 110 K using neutrons of wavelength 1.8 Å, integrated from $Q=2.5$ to $7\AA^{-1}$, is shown. In the middle frame is shown the theoretical intensity calculated from the bare PDOS of Singh and Du[15], convoluted with instrument resolution. At 1.6 K, the Bose factor leads to zero intensity for negative energy transfer, and measurements there serve to determine the background. The integrated intensity $I(Q) = \int d\omega I(Q,\omega)$ from the negative energy side, shown in the bottom frame, demonstrates the expected behavior for phonon scattering, which is approximately proportional.
FIG. 3: (color online) Top: \( I(\omega) = \int dQ S(Q, \omega) \) measured at 1.6 and 110 K. The integration range is from 2.5 to 7 \(^\AA\)^{-1}. Middle: Calculated bare intensity profile at 1.6 and 110 K. Bottom: Measured \( I(Q) = \int d\omega I(Q, \omega) \) at 1.6 and 110 K. The integration range is from -15 to -5 meV. The shaded profile is measured \( S(Q, \omega = 0) \). The peak positions of the bare PDOS of Singh and Du are well reproduced in the measured \( I(\omega) \). The calculated PDOS in \[21\] closely resembles that in \[15\]. Thus, the phonon spectra used in the electron-phonon coupling calculations in \[19, 21\], which do not favor the phonon mechanism for superconductivity in La(O,F)FeAs, have experimental support from this work.

Unconventional superconductivity mediated by various magnetic channels has been investigated theoretically \[14, 22, 23, 24, 25, 26, 27\]. Both \( d \)-wave and extended \( s \)-wave have been proposed for the superconducting order parameter of \( Ln(O,F)FeAs \). Korshunov and Eremin have investigated the consequences of these pairings in spin dynamics \[27\]. For \( d \)-wave pairing, the superconducting transition only modestly redistributes the spin spectral weight below 2\( \Delta_0 \), where \( \Delta_0 \) is the superconducting gap to \( Q^2 I(Q, \omega = 0) \) \[35\]. The peak positions of the bare PDOS of Singh and Du are well reproduced in the measured \( I(\omega) \). The calculated PDOS in \[21\] closely resembles that in \[15\]. Thus, the phonon spectra used in the electron-phonon coupling calculations in \[19, 21\], which do not favor the phonon mechanism for superconductivity in La(O,F)FeAs, have experimental support from this work.

In the right inset to the bottom frame of figure 4 magnetic neutron scattering intensity \( S(Q, \omega) \) measured in the superconducting state at 1.6 K is shown in the same \((\omega, Q)\) range as in the left inset. Below 2.5 meV, intensity is dominated by incoherent nuclear neutron scattering and is not shown. The energy dependence at the antiferromagnetic point is shown in the main bottom frame with the same energy scale as in the top frame. Above 2.5 meV, the Bose factor \( n(\omega, T) \approx 0 \) at 1.6 K. Thus, the peak positions of the bare PDOS of Singh and Du are well reproduced in the measured \( I(\omega) \). The calculated PDOS in \[21\] closely resembles that in \[15\]. Thus, the phonon spectra used in the electron-phonon coupling calculations in \[19, 21\], which do not favor the phonon mechanism for superconductivity in La(O,F)FeAs, have experimental support from this work.

For extended \( s \)-wave pairing, a strong resonance peak would appear at the nesting wavevector \( Q_{AFM}=(1/2,1/2,0) \) and \( \hbar \omega \sim 1.5 \Delta_0 \). In the left inset of the bottom frame and the top frame of Fig. 4 the theoretical imaginary dynamic spin susceptibility \( \chi''(Q, \omega) \) from \[27\] is shown for various cases. The value of \( \Delta_0 \) obtained from infrared measurements is between 3.1 and 3.7 meV \[28\], in the specific heat study 3.4(5) meV \[29\], and from tunneling 3.9(7) meV \[30\]. Therefore, the resonance peak at \( Q_{AFM} \) is between 4.4 and 6.9 meV.

In the right inset to the bottom frame of figure 4 magnetic neutron scattering intensity \( S(Q, \omega) \) measured in the superconducting state at 1.6 K is shown in the same \((\omega, Q)\) range as in the left inset. Below 2.5 meV, intensity is dominated by incoherent nuclear neutron scattering and is not shown. The energy dependence at the antiferromagnetic point is shown in the main bottom frame with the same energy scale as in the top frame. Above 2.5 meV, the Bose factor \( n(\omega, T) \approx 0 \) at 1.6 K. Thus,
the measured \( S(Q, \omega) \approx \chi''(Q, \omega) / \pi \) can be compared directly to the theoretical \( \chi''(Q, \omega) \) in Fig. 4. Powder averaging will enhance the measured intensity at \( Q \) larger than \( |Q_{AFM}| \) to some extent, however, the sharp resonance peak will be little affected.

We did not observe the strongly enhanced superconducting resonance peak in \( \text{LaO}_{0.87}\text{F}_{0.13}\text{FeAs} \) at 1.6 K. The upper limit for intensity of such a resonance peak is \( 0.5(1) \mu_B^2/\text{meV sr} / \text{per Fe from our data} \) (see the blue curve in the bottom frame). If the predicted resonance peak is as strong as in the unconventional superconductor \( \text{CeCoIn}_5 \), \( \sim 30 \mu_B^2/\text{meV sr} / \text{per Co} \), being two orders of magnitude stronger than our measurement limit, it would have been observed in our experiments. On the other hand, if the intensity of the resonance peak in \( \text{La}(\text{O,F})\text{FeAs} \) is similar to that in \( \text{YBa}_2\text{Cu}_3\text{O}_7\text{FeAs} \), it would not be observed in our measurements. Theoretically, the peak intensity for the resonance in \( \text{La}(\text{O,F})\text{FeAs} \) with the extended s-wave pairing depends on the choice of damping factor and corrections beyond the random-phase-approximation\[27\]. For the d-wave pairing also discussed in \[27\], the modest change in the spin dynamics would be beyond the sensitivity of this polycrystalline experiment.

In summary, the spin-density-wave order of \( \text{LaOFeAs} \) is displaced by superconductivity in \( \text{LaO}_{0.87}\text{F}_{0.13}\text{FeAs} \). The peaks in the theoretical phonon density of states at 12 and 17 meV are observed in our phonon measurements. The theory of phonon mediated superconductivity, which fails to produce the high \( T_C \approx 26 \text{ K} \), thus is based on reliable phonon calculation. Our experiments set an upper limit of \( 0.5 \mu_B^2/\text{meV sr} / \text{per Fe for the resonance peak in the spin excitations at the antiferromagnetic wavevector} \). Unconventional extended s-wave superconductivity mediated by spin fluctuations is constrained by the limit.

We would like to thank D. J. Singh and M.-H. Du for providing theoretical PDOS data. Work at LANL is supported by U.S. DOE, at USTC by the Natural Science Foundation of China, Ministry of Science and Technology of China (973 Project No: 2006CB601001) and by National Basic Research Program of China (2006CB922005). The DCS at NIST is partially supported by NSF under Agreement No. DMR-0454672.

* Electronic address: wbao@lanl.gov

[1] Y. Kamihara et al., J. Am. Chem. Soc. 128, 10012 (2006).
[2] T. Watanabe et al., Inorg. Chem. 46, 7719 (2007).
[3] Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008).
[4] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, arXiv:0803.3603.
[5] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, arXiv:0803.3790.
[6] Z. A. Ren, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, et al., arXiv:0803.4234.
[7] Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, arXiv:0803.4283.
[8] G. F. Chen, Z. Li, D. Wu, J. Dong, G. Li, W. Z. Hu, P. Zheng, J. L. Luo, and N. L. Wang, arXiv:0803.4384.
[9] P. Cheng, L. Fang, H. Yang, X. Zhu, G. Mu, H. Luo, Z. Wang, and H. H. Wen, arXiv:0804.0835.
[10] Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, et al., arXiv:0804.2053.
[11] R. H. Liu, G. Wu, T. Wu, D. F. Fang, H. Chen, S. Y. Li, K. Liu, Y. L. Xie, X. F. Wang, R. L. Yang, et al., arXiv:0804.2105.
[12] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, et al., arXiv:0803.3426.
[13] C. Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, et al., arXiv:0804.0795.
[14] M. A. McGuire, A. D. Christianson, A. S. Sefat, R. Jin, E. A. Payzant, B. C. Sales, M. D. Lumsdzen, and D. Mandrus, arXiv:0804.0796.
[15] D. J. Singh and M.-H. Du, arXiv:0803.0429.
[16] H. H. Wen et al., Europhys. Lett. 82, 17009 (2008).
[17] W. Lu, J. Yang, X. L. Dong, Z. A. Ren, G. C. Che, and Z. X. Zhao, arXiv:0803.4266.
[18] B. Lorentz, K. Sasmal, R. P. Chaudhury, X. H. Chen, R. H. Liu, T. Wu, and C. W. Chu, arXiv:0804.1582.
[19] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, arXiv:0804.2740.
[20] K. Haule, J. H. Shim, and G. Kotliar, arXiv:0803.1279.
[21] L. Boeri, O. V. Dolgov, and A. A. Golubov, arXiv:0803.2703.
[22] K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, arXiv:0803.3325.
[23] X. Dai, Z. Fang, Y. Zhou, and F. Zhang, arXiv:0803.3982.
[24] Q. Han, Y. Chen, and Z. D. Wang, arXiv:0803.4346.
[25] H. Eschrig, arXiv:0804.0186.
[26] P. A. Lee and X. G. Wen, arXiv:0804.1739.
[27] M. M. Korshunov and I. Eremin, arXiv:0804.1793.
[28] G. F. Chen, Z. Li, G. Li, J. Zhou, D. Wu, J. Dong, W. Z. Hu, P. Zheng, Z. J. Chen, J. L. Luo, et al., arXiv:0803.0128.
[29] G. Mu, X. Zhu, L. Fang, L. Shan, C. Ren, and H. H. Wen, arXiv:0803.0928.
[30] L. Shan, Y. Wang, X. Zhu, G. Mu, L. Fang, and H. H. Wen, arXiv:0803.2405.
[31] H. Yang, X. Zhu, L. Fang, G. Mu, and H. H. Wen, arXiv:0803.0623.
[32] X. Zhu, H. Yang, L. Fang, G. Mu, and H. H. Wen, arXiv:0803.1288.
[33] A. Larson and R.B. Von Dreele, GSAS: Generalized Structure Analysis System, (Los Alamos National Laboratory, 1994).
[34] T. Yildirim, arXiv:0804.2252.
[35] R. Osborn et al., Phys. Rev. Lett. 87, 017005 (2001).
[36] C. Stock et al., Phys. Rev. Lett. 100, 087001 (2008).
[37] S. M. Hayden, H. A. Mook, P. Dai, T. G. Perring, and F. Doğan, Nature 429, 531 (2004).