Probing superconductivity and pairing symmetry by coherent phonons in multiorbital superconductors

Chandan Setty, 1 Jinmin Zhao, 2 and Jiangping Hu 2,1,3,4

1 Department of Physics and Astronomy, Purdue University, West Lafayette, Indiana 47907, USA
2 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100090, China
3 Collaborative Innovation Center of Quantum Matter, Beijing, China

We show that the phase information contained in coherent phonon oscillations generated by a laser pulse in a multi-orbital superconductor can be used as an experimental tool to probe superconductivity and pairing symmetries. The phase difference between the normal and superconducting states is proportional to the superconducting order parameter just below the superconducting transition temperature, \(T_c\). It also exhibits different behaviors for superconducting states with different pairing symmetries. In particular, if there is an orbital-dependent internal sign change state, the phase difference can have a discontinous jump below \(T_c\).

Introduction: The superconductivity in a multi-band electronic system can be extremely rich and complex. Many recently discovered correlated electron systems belong to this category of multi-band superconductors. For example, iron-based superconductors discovered six years ago[1] have multiple Fermi surfaces and their bands near the Fermi level are attributed to all five \(d\)-orbitals. These materials exhibit a variety of intriguing properties associated with all of the degrees of freedom including charge, orbital, spin and lattice[2], which can, in principle, lead to many possible novel superconducting states[3].

While theoretically, a multi band structure is a fertile ground for new physics, in experiments, it is still very difficult to detect them and determine their mechanisms because of the involvement of the multi-degrees of freedom. Many experimental observations can be subject to multiple interpretations; for example, in iron-based superconductors[4], the interplay among electronic nematicity, magnetism and orbital ordering is still a subject of active research[5, 6]. The pairing symmetry of the superconducting state, arguably the most important property, is still controversial and highly debated[3]. While the magnitude of the superconducting order parameter can be directly probed by many experimental techniques, such as angle-resolved photoemission spectra (ARPES) and scanning tunneling microscopy(STM), there are few good direct probes to the phase distribution of the superconducting order parameter across their multiorbital Fermi surface. In particular, when the phase distribution is not enforced by the symmetry of the superconducting state, as the case stands in many theoretically proposed states in iron-based superconductors, the phase sensitive junction techniques[7] that determined the \(d\)-wave pairing symmetry in cuprates is also not applicable.

Since the last couple of decades, ultrafast pump-probe spectroscopy has played an increasing role in probing the superconducting ground state, with the high \(T_c\). Cuprates having grabbed much of the attention[8–27], along with a few experiments performed on multiorbital iron superconductors[28–36] as well. The primary focus of most of these experiments has been the measurement of relaxation times that can be extracted from the behavior of the change in reflectivity \(\frac{\Delta R}{R}\) of the probe pulse as a function of the delay time \(\delta\) between the pump and the probe. From this, one can indirectly obtain information about the strength of the electron-phonon couplings and their anisotropies[11, 12], density of photoexcited quasi-particles[13, 25], pseudo and superconducting gaps[25], and signatures of the origin of the superconducting interaction[13]. However, even though coherent phonon oscillations in ultrafast experiments have been generated[14, 36] and studied[32, 34] for a while now, only a few experimental works address the role of the superconducting phase on these oscillations and no theoretical background has been laid.

In this Letter, we show that the phase of these coherent phonon oscillations contains useful information about the superconducting phase and its pairing symmetry; in particular, we show that the difference in the phase of the oscillations between the normal and superconducting state is proportional to the superconducting gap, and in certain scenarios, can help distinguish the sign change of superconducting orders on different bands. Thus, the coherent phonons can act as a new experimental probe of superconducting symmetries.

The coherent phonon amplitude mode with wave vector \(q\) is described by the driven harmonic oscillator[37, 38]

\[
\frac{d^2Q_q}{dt^2} + 2\beta \frac{dQ_q}{dt} + \Omega^2 Q_q = F(t)
\]

(1)

where \(Q_q\) is the amplitude of the phonon mode, \(\Omega\) is the frequency of the oscillator, \(\beta\) is the damping parameter and \(F(t)\) is the driving force. The solution to the above equation is given by

\[
Q_q(t) = Ae^{-\beta t}\cos(\tilde{\Omega}t + \Gamma ph)
\]

(2)

where \(\tilde{\Omega} = \sqrt{\Omega^2 - \beta^2}\) and \(A\) is the amplitude of the oscillation which is proportional to the magnitude of the
driving force $F$. For simplicity, we will ignore any effect of damping. In such a case, the phase of the phonon oscillation $\Gamma_{ph}$ is given by \ref{eq:3}:

$$\tan(\Gamma_{ph}) = \frac{Im(iF(\omega))}{Re(iF(\omega))}.$$ \hfill (3)

The driving force $F(t)$ can be derived microscopically under reasonable approximations. Consider a general Hamiltonian that describes the physical processes in an ultrafast pump-probe experiment given by

$$H = H_e + H_p + H_{e-p} + H_{e-i}(t),$$ \hfill (4)

where $H_e$, $H_p$, $H_{e-p}$ and $H_{e-i}(t)$ are electronic, phononic, electron-phonon coupling and electron-pulse interaction parts respectively. In a superconducting state, the electronic part, $H_e$, is given by the general BCS form

$$H_e = \sum_{k \sigma \alpha} \epsilon_{k \sigma} c_{k \sigma \alpha}^{\dagger} c_{k \sigma \alpha} + \frac{1}{2} \sum_{k} \Delta c_{k \alpha}^{\dagger} c_{-k \alpha}^{\dagger}.$$ \hfill (5)

where $\alpha$ and $\sigma$ are the orbital and spin index. We take the standard form for $H_p = \frac{1}{2} \sum_{q} (P_q^2 + Q_q^2)$ and $H_{e-p} = \sum_{kq\sigma \alpha} \epsilon_{q \sigma} V_{q \sigma}(t) c_{k \sigma \alpha}^{\dagger} c_{k+q \sigma \alpha} + h.c$. Here $Q_q$ and $P_q$ are the canonical coordinates and momenta. The time dependent electron-laser pulse interaction is given by $H_{e-i}(t) = \sum_{kq\sigma \alpha} V_{q \sigma}(t) c_{k \sigma \alpha}^{\dagger} c_{k+q \sigma \alpha}$ with $V_{q \sigma}(t) = \frac{1}{\hbar c} \int d\tau \phi_{q \sigma}(\tau) [\tilde{A}(\tau) \cdot \tilde{p}] \phi_{q \sigma}(\tau)$. As the coherent phonons are generated at $q = 0$ and the momentum of the light is much smaller than the electron momentum, we can set $q = 0$ in all above Hamiltonians.

We consider parameters in a typical femtosecond pump-probe experiment. The pump pulse (central frequency $\omega_o \sim 375 THz$) has a width of $\tau \sim 80 fs$ and a relatively broad spectral width of the order of $\Delta \nu \sim 5 - 10 THz$. Such a spectral width is just enough to excite the lowest energy optical phonon mode whose energy is around $\Omega \sim 5 THz$. To ensure that the phonon oscillations are properly resolved in time, the width of the pump laser pulse satisfies the condition $\tau << \Omega^{-1}$.

The average force driving the coherent phonon oscillations is given by $F(t) = -\partial (H_{e-p}(t))/\partial Q_{\tilde{q}}$. Here, $\langle ... \rangle$ denotes an ensemble average over eigen states of $H - H_{e-i}(t)$ time evolving in $H_{e-i}(t)$ perturbatively. In lines with the authors in ref \ref{eq:3}, we assume that the electric field is spatially homogeneous and a gaussian centered around $\omega_o$. Thus the electric field product $E(\omega)E(\omega + \Omega)$ is strongly peaked at $\omega_o = \Omega/2$. This leads to an expression for the driving force\ref{eq:3}:

$$F(\Omega) = \frac{-C}{(\omega_o - \Omega^2)} \sum_{k \sigma \alpha} \left( \frac{\langle \xi_{n,m}(\tilde{k}) \bar{V}_{nm}(\tilde{k}) \rangle}{(\omega_{nl} - \Omega - i\gamma)(\omega_{nl} - \omega_o - i\gamma)} + \frac{\xi_{n,m}(\tilde{k}) \bar{V}_{nm}(\tilde{k})}{(\omega_{nl} + \Omega + i\gamma)(\omega_{nl} - \omega_o + i\gamma)} \right).$$ \hfill (6)

Here $n, m, I$ are band states, $C$ is an unimportant constant, $g$ contributes to the optical absorption, and $\tilde{k}$ is the crystal momentum. We have defined $\omega_{nl} \equiv \omega_{nl}(\tilde{k}) = \omega_n - \omega_l$, where $\omega_n$ is the energy of band $n$ with momentum $\tilde{k}$. The tilde sign above the matrix elements denotes the respective quantities written in the band basis. In the expression for $F(\Omega)$, we have assumed that the laser frequency is the largest energy scale in the problem. Therefore, we have chosen to keep the most resonant terms by ignoring a third term which has a denominator proportional to $\omega_o^2$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{A cartoon plot showing the toy band structure used to illustrate the scattering between superconducting bands close to the Fermi level. A quasiparticle is light scattered (solid wavy line) from an occupied band state $a$ to an empty state in band state $b$ and light scattered again from band state $b$ to another band state $c$. Finally the quasiparticle makes a transition back to the band state $a$ by scattering with a phonon (dashed-dotted line). The energy scale on the vertical axis is of the order of the superconducting gap.}
\end{figure}
force, \( F(t) = -\partial (H_{s-p})(t)/\partial Q_\phi \).

We now proceed with our calculation of the average driving force \( F(t) \). To bring out the physics essential for our discussion, we consider a scattering process illustrated in the cartoon in Fig 1. A quasiparticle in the state \( a \) is scattered by a photon to the empty state \( b \) above the Fermi level, and then scattered again into another empty state \( c \) through a second photon. Finally, the quasiparticle is scattered back to its original state \( a \) through a process that can be determined analogously. To do this, we first have to perform an unitary transform into the orbital basis and then use the formulas described in [39] for tight binding matrix elements. We can write the above matrix element product as

\[
\tilde{\xi}_{ac} V_{cb}(\vec{k}) V_{ba}(\vec{k}) = \Delta \frac{f(\theta_k)}{x_+^2 + x_-^2} (\epsilon_+^2 + \epsilon_-^2) (\epsilon_+^2 - \epsilon_-^2) - \Delta^2 \right) \times \left[ (\epsilon_+^2 - \Delta^2) + \Delta \sin 2\theta_k (2\Delta \epsilon_-) \right],
\]

where \( f(\theta_k) = -(\partial m_k)^2 \cos^2 2\theta_k \), \( x_\pm = \sqrt{\Delta^2 + \epsilon_\pm^2} \), \( \epsilon_\pm = \epsilon_\pm(\vec{k}) + E_\pm(\vec{k}) \), with the band angle \( \tan 2\theta_k = 2m_k/(\epsilon_{1k} - \epsilon_{2k}) \), \( \epsilon_\pm(\vec{k}) \) the band energies, and \( E_\pm(\vec{k}) = \sqrt{\Delta^2 + \epsilon_\pm^2(\vec{k})^2} \). From the above expression for the matrix element product, we can separate the most dominant contributions from different regions of the Brillouin zone. We consider three different cases: (1) contributions from momentum space points far away from the Fermi surface where \( \epsilon_\pm(\vec{k}) >> |\Delta| > 0 \), (2) on the Fermi surface \( \epsilon_\pm(\vec{k}) = 0 < |\Delta| << \epsilon_\pm(\vec{k}) \) and finally, (3) on the Fermi surface \( \epsilon_\pm(\vec{k}) = 0 < |\Delta| << \epsilon_\pm(\vec{k}) \). We find that

\[
\tilde{\xi}_{ac} V_{cb}(\vec{k}) V_{ba}(\vec{k}) = f(\theta_k) \times \left\{ \begin{array}{ll}
\frac{|\Delta|}{\epsilon_+} & \epsilon_+ > > |\Delta| > 0 \\
\frac{2|\Delta|}{\epsilon_+} \epsilon_- & \epsilon_- > > |\Delta| > 0 = \epsilon_+ \\
\frac{2|\Delta|}{\epsilon_-} \epsilon_+ & \epsilon_+ > > |\Delta| > 0 = \epsilon_-, 
\end{array} \right.
\]

where we have defined the effective band energy \( \epsilon = \frac{\epsilon_+ \epsilon_-}{\epsilon_+ + \epsilon_-} \) and \( \epsilon_{2\theta} = \sin 2\theta_k \). Similar expressions can be obtained for the other scattering processes. The energy denominators appearing in the expression for the driving force in eq [10] depend quadratically on the energy gap. From this, along with the expression for the matrix element product (written in eq [8]), we arrive at the central result of this section — the coherent phonon phase encodes the behavior of the superconducting order parameter. For small \( \Delta \), the phase can be written very generally as \( \Gamma_{ph} = \alpha_1 + \alpha_2 \Delta(T) \), where \( \alpha_1 \) and \( \alpha_2 \) are constants independent of temperature. As a result, the phase difference between the superconducting and normal state is proportional to the pairing gap. We also additionally conclude that the contribution to the average driving force from the momentum points far away from the Fermi surface is of \( O(\Delta/\ell) \) smaller than the contribution from those close to the Fermi surfaces. However, all the regions in the Brillouin zone contribute to the phase of the oscillation to the same order. This naturally implies that for a significant driving force to be generated, we would require the frequency of the phonon mode excited (\( \sim 5 - 10 THz \)) to be of the order of the superconducting gap. This is a condition that is hard to attain in classic BCS superconductors, but is comfortably satisfied by high \( T_c \) Cuprates and iron based superconductors.

b) Three band case: To further test the above results, we consider a more realistic band model that describes iron based superconductors and study the pairing symmetry dependence. We also examine any signatures that can capture the inter-orbital sign change contained in the phase of coherent phonon oscillation. To illustrate our numerical results and maintain analytical tractability, we choose the three band model proposed by Daghofer et.al [40]. Fig 2 shows our result for the temperature dependence plot of the phase difference \( \Gamma_S - \Gamma_N \) between the superconducting and normal states across \( T_c \). The phase is a constant above \( T_c \) and varies below it due to the development of a superconducting gap on the Fermi surfaces. For a simple constant \( s- \) wave pairing (Fig 2 (Left)), the variation of the phase in the SC state is maximum at \( T = 0 \) (for small values of the gap) and follows a linear dependence on \( \Delta \), as was analytically derived in the previous section. However, on increasing the magnitude of \( \Delta \), the change in phase develops a maximum at a temperature \( 0 < T < T_c \) and then falls off at \( T = 0 \) due to higher order contributions of \( \Delta \). Fig 2 (Right) shows the plot of the phase of the oscillation as a function of temperature for different pairing symmetries. For the \( s- \) wave cases, there is a substantial change in

![FIG. 2. Plot showing the variation of the phase(\( \Gamma_{ph} \)) difference between superconducting(8) and normal(\( \Gamma_N \)) state as a function of temperature across \( T_c \). (Left) Phase as a function of magnitude of a constant \( s- \) wave gap on all the three bands. (Right) Phase for different pairing forms of the gap, all the same on the three bands. The values of the electron phonon coupling is chosen as \( \xi' = 0.4eV \) for interorbital, \( \xi'/4 \) for \( xx/yz \) and \( \xi'/2 \) for \( xy \) intraorbital coupling and the damping coefficient is chosen as \( g = 0.3eV \). The laser and phonon frequencies are fixed at 2eV and 0.2eV respectively.](http://example.com/fig2.png)
Therefore, has a $\pi$ discontinuity in the phase. On the other hand, in the (++) scenario, the real part of $iF$ does not change sign and results in a smooth variation of phase with temperature (see fig 3 (bottom row)).

To get the physics governing the numerics above, we consider the three band model with a definite sign of the gap on the $xz$ and $yz$ orbitals (denoted by $\Delta_1 = \Delta$ and $\Delta_2 = \Delta$) and an arbitrary gap $\Delta_3$ on the $xy$ orbital. We find that for small values of $\Delta_3$, the driving force on the phonons can be written as

$$F(T) = \sum_k \left( \tilde{\alpha}_1(k) + s\text{gn}(\Delta_3 K) \tilde{\beta}_1(k)|\Delta_3(T)| \right) + i \left( \tilde{\alpha}_2(k) + s\text{gn}(\Delta_3 K) \tilde{\beta}_2(k)|\Delta_3(T)| \right).$$

Here, $\tilde{\alpha}_i$ and $\tilde{\beta}_i$ are band structure dependent functions which can be determined for a given model. For the above model, we find that $\sum_k \tilde{\alpha}_2(k)$ and $\sum_k \tilde{\beta}_2(k)$ are both negative. This implies that when all the three orbitals have the same sign of the gap, the real part of $iF(T)$ is negative. On the other hand, if the sign change exists among the third orbitals, the denominator becomes zero for a critical temperature and results in an observable $\pi$ phase jump.

The above results can be applied to investigate the pairing symmetries in multi-orbital superconductors. Here we specifically discuss its applications to iron-based superconductors. Different pairing symmetries, including $s$-wave\textsuperscript{41–46} and $d$-wave pairing symmetries\textsuperscript{47, 48}, were proposed for different families of iron-based superconductors. Even within the $s$-wave pairing symmetry, there are a variety of possibilities on the internal sign changes, including the sign changes between different pockets (so called $s^\pm$\textsuperscript{41–44}) and between bands featured by different orbitals (so called orbital-dependent $s^\pm$ or antiphase-$s^\pm$\textsuperscript{49, 52}). Our results suggest that the phase of coherent phonons should have distinct behaviors with respect to the $s\pm$, antiphase-$s^\pm$ and $d$-wave states. In particular, as shown in fig 3 if a phase jump can be observed below $T_c$, it should be a smoking-gun signature for the antiphase-$s^\pm$ state.

Conclusions: We have shown that coherent phonon oscillations can be an experimental probe of the superconducting state and its pairing symmetry. The phase of the coherent phonon carries intrinsic information of superconducting order parameters and can be applied to determine the pairing symmetries in complex multi-orbital superconductors.

JPH acknowledges support from grants: MOST of China (2012CB821400, 2015CB921300), NSFC(11190020, 91221303, 11334012) and “Strategic Priority Research Program (B)” of the Chinese Academy of Sciences( XDB07020200). JMZ is supported by NSFC (11274372) and MOST of China (2012CB821402).
[1] Y. Kamihara et al., Journal of the American Chemical Society 130, 3296 (2008).
[2] D. C. Johnston, Advances in Physics 59, 803 (2010).
[3] P. Hirschfeld et al., Reports on Progress in Physics 74, 124508 (2011).
[4] G. Stewart, Reviews of Modern Physics 83, 1589 (2011).
[5] R. Fernandes et al., Nature physics 10, 97 (2014).
[6] P. Dai et al., Nature Physics 8, 709 (2012).
[7] D. Van Harlingen, Reviews of Modern Physics 67, 515 (1995).
[8] R. A. Kaindl et al., Physical Review B 72, 060510 (2005).
[9] C. Giannetti et al., Physical Review B 79, 224502 (2009).
[10] R. Saichu et al., Physical review letters 102, 177001 (2009).
[11] L. Perfetti et al., Physical review letters 99, 197001 (2007).
[12] F. Carbone et al., Proceedings of the National Academy of Sciences 105, 20161 (2008).
[13] M. Schneider et al., EPL (Europhysics Letters) 60, 460 (2002).
[14] W. Albrecht et al., Physical review letters 69, 1451 (1992).
[15] P. Kusar et al., Physical review letters 101, 227001 (2008).
[16] G. Bianchi et al., Physical review B 72, 094516 (2005).
[17] P. Kusar et al., Physical Review B 72, 014544 (2005).
[18] E. E. Chia et al., Physical review letters 99, 147008 (2007).
[19] V. V. Kabanov et al., Physical review letters 95, 147002 (2005).
[20] J. Hinton et al., Physical Review B 88, 060508 (2013).
[21] C. Stevens et al., Physical review letters 78, 2212 (1997).
[22] N. Gedik et al., Physical Review B 70, 014504 (2004).
[23] G. P. Segre et al., Physical review letters 88, 137001 (2002).
[24] N. Gedik et al., Science 300, 1410 (2003).
[25] V. Kabanov et al., Physical Review B 59, 1497 (1999).
[26] D. Dvorsek et al., Physical Review B 66, 020510 (2002).
[27] J. Demsar et al., Physical review letters 82, 4918 (1999).
[28] C. Bonavolont et al., Superconductor Science and Technology 26, 075018 (2013).
[29] C. Luo et al., New Journal of Physics 14, 103053 (2012).
[30] C. Luo et al., Physical review letters 108, 257006 (2012).
[31] E. E. Chia et al., Physical review letters 104, 027003 (2010).
[32] S. Kumar et al., EPL (Europhysics Letters) 100, 57007 (2012).
[33] B. Mansart et al., Physical Review B 82, 024513 (2010).
[34] B. Mansart et al., Physical Review B 80, 172504 (2009).
[35] T. Mertelj et al., Physical review letters 102, 117002 (2009).
[36] H. Takahashi et al., Journal of the physical society of Japan 80 (2011).
[37] R. Merlin, Solid State Communications 102, 207 (1997).
[38] D. M. Riffe and A. Sabbah, Physical Review B 76, 085207 (2007).
[39] T. G. Pedersen et al., Physical Review B 63, 201101 (2001).
[40] M. Daghofer et al., Physical Review B 81, 014511 (2010).
[41] I. Mazin et al., Physical Review Letters 101, 057003 (2008).
[42] K. Kuroki et al., Physical Review Letters 101, 087004 (2008).
[43] A. V. Chubukov et al., Physical Review B 78, 134512 (2008).
[44] R. Thomale et al., Physical review letters 101, 206404 (2008).
[45] C. Fang et al., Physical Review X 1, 011009 (2011).
[46] H. Kontani and S. Onari, Physical review letters 102, 147001 (2009).
[47] R. Thomale et al., Physical review letters 107, 117001 (2011).
[48] T. Maier et al., Physical Review B 83, 100515 (2011).
[49] X. Lu et al., Physical Review B 85, 054505 (2012).
[50] N. Hao and J. Hu, Physical Review B 89, 045144 (2014).
[51] J. Hu, Physical Review X 3, 031004 (2013).
[52] Z. Yin et al., Nature Physics 10, 845 (2014).