Critical Charge Fluctuations in Iron Pnictide Superconductors

V. K. Thorsmølle, M. Khodas, Z. P. Yin, Chenglin Zhang, S. V. Carr, Pengcheng Dai, G. Blumberg

1Department of Physics & Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA.
2Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa 52242, USA.
3Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel.
4Department of Physics and Astronomy, Rice University, Houston, Texas 77005, USA.
5Department of Physics, University of Tennessee, Knoxville, Tennessee 37996, USA.

*To whom correspondence should be addressed, e-mails: girsh@physics.rutgers.edu

The multiband nature of iron pnictides gives rise to a rich temperature-doping phase diagram of competing orders and a plethora of collective phenomena. At low dopings, the tetragonal-to-orthorhombic structural transition is closely followed by a concomitant spin density wave transition both being in close proximity to the superconducting phase. A key question is the microscopic mechanism of high-\(T_c\) superconductivity and its relation to orbital ordering and magnetism. Here we study the NaFe\(_{1-x}\)Co\(_x\)As superconductor using polarization resolved Raman spectroscopy. The Raman susceptibility shows critical non-symmetric charge fluctuations across the entire phase diagram associated with a hidden ordered state. The charge fluctuations are interpreted in terms of plasma waves of quadrupole intra-orbital excitations in which the electron and hole Fermi surfaces breath in-phase. Below \(T_c\), these plasmons undergo a metamorphosis into a coherent ingap mode of extraordinary strength and at the same time serve as a glue for non-conventional superconducting pairing.
An important aim in the study of iron-based superconductors is to elucidate the mechanism of electron pairing responsible for superconductivity and its relation to adjacent phases (1–3). Most FeAs compounds share a common phase diagram which in the underdoped region is marked by a tetragonal-to-orthorhombic structural transition at $T_S$ followed by a magnetic ordering transition at $T_{SDW}$ of collinear spin stripes which either precedes or coincides with $T_S$ (4, 5). Here, spin susceptibility and relaxation rate $1/T_1 T$ demonstrate critical enhancement upon approaching the SDW transition (6–8). On introducing dopant atoms, superconductivity emerges with a transition temperature $T_c$ of tens of degrees (1). At these dopings, the spin susceptibility data show that when going away from the SDW phase the enhancement is rapidly suppressed (9–13). While the close proximity to magnetic order naturally favors spin fluctuations as a candidate in providing the glue for Cooper pairs (3), suppressed spin fluctuations appear to be insufficient in explaining the whole temperature-doping ($T−x$) phase diagram (SOM, Fig. S1).

So far, no clear consensus has been reached on the symmetry of the superconducting order parameter (OP). Theories building on spin fluctuations favor unconventional $s^\pm$ pairing in which the superconducting OP changes sign between electron- and hole-like FSs (14). Yet, other theories embrace orbital fluctuations building on superconductivity with $s^{++}$-pairing in which there is no sign change (15). Recently, orbital antiphase $s^\pm$ has been proposed in which the pairing function of the Fe $d_{xy}$ orbital has opposite sign to the $d_{xz}$ and $d_{yz}$ orbitals (16), as well as orbital triplet pairing (17). Experimentally, scanning tunneling microscopy (STM) sensitive to quasiparticle interference infers an OP with sign-reversal (18). INS measurements have inferred $s^\pm$-pairing in BaFe$_{2−x}$Co$_x$As$_2$ (19) or NaFe$_{0.935}$Co$_{0.045}$As (13). Heat transport measurements on Ba(Fe$_{1−x}$Co$_x$)As$_x$ (20) and thermal conductivity measurements on (Ba,K)Fe$_2$As$_2$ (21) and BaFe$_2$(As$_{1−x}$P$_x$)$_2$ (22) are suggestive of accidental nodes. These results were interpreted in terms of competing pairing interactions with a crossover from an $s$–wave to $d$–wave OP (21) or $s^\pm$ to $s^{++}$ with doping or increased impurity level.

Here we use polarization-resolved electronic Raman spectroscopy to study the temperature,
frequency and doping dependence of the Raman susceptibility of NaFe\textsubscript{1−x}Co\textsubscript{x}As in the normal and superconducting state. In a wide range of temperatures and dopings above the $T_S(x)$ and $T_c(x)$ lines we find that the normal state properties are governed by the emergence of collective charge fluctuations of $XY$–symmetry displaying critical behavior upon cooling with the system striving to reach an orbitally-ordered state with broken four-fold rotational $C_4$–symmetry at the hidden temperature $T_0(x)$. In the low doping region, the formation of the pursued ordering is intervened by the structural transition which is characterized by doubling of the unit cell and a gapped density wave (DW) state. At higher dopings the orbital ordering is prohibited by the superconducting phase, but the fluctuations serve as the pairing glue. In the lowest temperature limit, all of the $T_0(x)$, $T_S(x)$, and $T_{SDW}(x)$ lines come close together at a critical doping $x_c$ within close proximity of maximum $T_c (\approx 20$ K (23)) signifying competition of the OPs. The critical fluctuations are interpreted as collective plasma waves of quasiparticle intra-orbital excitations. Below $T_c$, the critical plasmons undergo a metamorphosis into extraordinarily strong and sharp ingap modes. At the same time, the plasmons serve as glue for unconventional $s^\pm$ superconducting pairing.

Angle-resolved photoemission spectroscopy (ARPES) reveals five FSs in NaFeAs, three hole FSs $\gamma$, $\alpha$ and $\beta$ surrounding the $\Gamma$-point and two electron FSs $\delta$ and $\epsilon$ centered at the M-point, Fig. 1C (24). The orbital content of the larger $\gamma$ FS is mainly composed of $d_{xy}$ orbitals, while the $\alpha$ and $\beta$ FSs primarily have $d_{xz}$ and $d_{yz}$ orbital character. At the M point, the inner (outer) part of the $\delta/\epsilon$ FS has $d_{xz}$ and $d_{yz}$ ($d_{xy}$) orbital character. The $d_{xz}$ and $d_{yz}$ bands are degenerate in the tetragonal phase. However, starting close to $T_S$, their occupation degeneracy is lifted with a splitting which amounts to $\approx 35$ meV at low temperatures (24, 25).

Doping NaFeAs with Co is an isovalent substitution with Fe in which the overall charge of the two cations are kept constant. However, it controls the orbital content and changes the sizes of the electron and hole pockets which has profound impacts on the physical properties (26). For NaFeAs, the $\Gamma$ hole pocket and the outer part of the $\delta/\epsilon$ electron pocket are shown to have near-equal sizes promoting nesting between the holes and electrons, Fig. 1C. With Co-doping,
shown in Fig. 1D, the bands shifts downward with respect to the Fermi level $E_F$ and the $\alpha$ and $\beta$ hole pockets eventually vanishes below the Fermi level (26). The $\gamma$ hole pocket becomes smaller while the $\delta/\epsilon$ electron pocket grows in size which will consequently cause a gradually vanishing nesting.

The temperature or doping dependent electronic Raman susceptibility $\chi''(\omega, T, x)$ reveals the dynamics of collective excitations and provides an unambiguous identification of their symmetry. In contrast to other symmetry sensitive probes requiring external perturbations, as strain field (7, 27) or magnetic techniques (6, 9–12, 28), the photon field used in Raman spectroscopy is weak and as such presents an ideal tool to study the dynamics and symmetry of fluctuations and collective excitations without introducing external perturbations (29–32).

The Raman response function is sensitive to charge density fluctuations driven by the incident and scattered photon fields. For a given scattering geometry with polarization vectors $\mathbf{e}^I$ and $\mathbf{e}^S$ for the incident and scattered photons, the Raman susceptibility is given by,

$$\chi_{I,S}(\omega) \propto -i \int_0^{\infty} e^{i\omega t} \langle [\tilde{\rho}^{I,S}(t), \tilde{\rho}^{I,S}(0)] \rangle \, dt. \quad (1)$$

In the effective mass approximation, $\tilde{\rho}^{I,S} = \sum_{i,j} e_{I,i} e_{S,j} \sum_b \mathbf{R}_{i,j}^b \hat{n}_b(\mathbf{k})$, where $\mathbf{R}_{i,j}^b(\mathbf{k}) = \frac{m}{2\hbar^2} \frac{\partial^2 \epsilon_b(\mathbf{k})}{\partial k_i \partial k_j}$ is the inverse effective mass tensor, $m$ denotes the electron mass, and $\hat{n}_b(\mathbf{k})$ the occupation of the Bloch state at momentum $\mathbf{k}$ in the band $b$ with dispersion $\epsilon_b(\mathbf{k})$ (33, 34).

The Raman response, eq. (1) of a normal plasma represents a broad featureless continuum (35). In the BCS single band $s$-wave superconductor the response is non-zero only for $\omega > 2\Delta$, and is marked by the square root divergence at $\omega = 2\Delta$, (29). In addition, if a non-$s$-wave Cooper channel is attractive, the Bardasis-Schrieffer mode forms below $2\Delta$. These modes are excited by photons only indirectly as a transformation of a particle-hole ($p$-$h$) into a Cooper pair requires assistance of the condensate (36, 37). The very same reasoning implies that $p$-$h$ and particle-particle ($p$-$p$) are inseparable in the presence of a condensate. This statement does not apply to multiband superconductors with sign changing gap (38).

In multiband superconductors we differentiate between weak and strong interband interac-
tions. In the first scenario, which applies to MgB$_2$, the low energy Leggett mode results from coherent Cooper pair interband tunneling \((30, 39, 40)\). Here we focus on the second possibility, which applies to NaFe$_x$Co$_{1-x}$As, where the Leggett mode is pushed above \(2\Delta\) and is undetectable. Instead, \(p-h\) rather than Cooper pairs were proposed to form a bound exciton in \(A_{1g}\) symmetry consistent with an \(s^\pm\)-wave symmetric condensate. This \(p-h\) exciton, \(\omega_{p-h}^{A_{1g}}\) is represented by in-phase breathing of the electron and hole FSs. Such a breathing mode entails charge transfer between the two pockets (Fig. 7B and fig. S2B) and turns the repulsion into an effective attraction \((41)\) similar to the reasoning leading to \(s^\pm\) superconductivity. This similarity implies that the intra-pocket repulsion is detrimental to \(\omega_{p-h}^{A_{1g}}\) \((30, 41)\). Here we demonstrate that a different hitherto unknown \(B_{2g}\) \(p-h\) exciton is the strongest spectroscopic feature in the entire superconducting domain.

The symmetrized Raman tensor \(\chi_{I,S}(\omega)\) for the different scattering geometries can be classified by the irreducible representations for the crystallographic point group \((42)\). The incident and scattered photon fields cross polarized along the \(a\)- and \(b\)-directions of the two-Fe unit cell yields \(\chi_{XY}\) susceptibility. For NaFe$_x$Co$_{1-x}$As with \(D_{4h}\) point group symmetry in the tetragonal phase, \(\chi_{XY}\) probes excitations in \(B_{2g}\) symmetry. The cross polarized photon fields rotated by \(45^\circ\) yields \(\chi_{xy}\) or \(B_{1g}\) susceptibility. \(\chi_{A_{1g}}\) can be obtained in two steps: first, by aligning both photon fields along one axis, and then by obtaining the \(xy\) susceptibility. \(\chi_{A_{1g}}\) is given by \(\chi_{XX}-\chi_{xy}\). We used a laser excitation energy of \(\omega_L=2.6\) eV, except for investigations of the ingap collective modes shown in Fig. 7 where \(1.93\) eV was also used. Pre-resonant \(1.93\) eV provides excitations for the study of both particle-particle (\(p-p\)) as well as \(p-h\) excitons.

In real space, local electron-hole excitations between \(d_{xz}\) and \(d_{yz}\) orbitals on an Fe-site lead to charge transfers as illustrated in Fig. 1F. This induces a quadrupole moment in \(B_{2g}\) \((XY)\) symmetry with the nodes along the \(X-Y\) directions. The resulting \(B_{2g}\) excitation can be a singlet with no spin flip, or a triplet with spin flip. However, an excitation with a spin flip excites a magnon which does not couple to light in the leading order.

In momentum space, modulations of the FSs around the \(\Gamma\)- and M-point with nodes along
ΓX and ΓY represent a neutral quadrupole charge density excitation. Here we explain *all* our data assuming only that the energy is minimized if the above two FSs undergo in-phase, $d^{\pm}$ quadrupole deformations, Figs. 1F and figs. S3,S4. This assumption holds when the interband $d$-wave repulsion dominates the intraband interactions. The synchronization of the two FSs ensures an effective attraction in the $d$-wave $p$-$h$ channel similar to the Cooper channel (14).

In Fig. 2 we show Raman susceptibility $\chi''_{I,S}(\omega)$ at representative temperatures and dopings for the $A_{1g}$, $B_{2g}$ and $B_{1g}$ symmetry channels to point out important features in relation to the tetragonal, orthorhombic, SDW and superconducting phases of the $T$–$x$ phase diagram (Fig. 3A) which will be discussed in depth below. Most of these features are reflected in the $\chi''_{B_{2g}}$ response, while $\chi''_{A_{1g}}$ contains important characteristics of superconducting nature, and $\chi''_{B_{1g}}$ mainly features a $B_{1g}$ phonon. The detailed temperature and doping dependence is shown in Figs. 4-6.

Using Kramers-Kronig transformation, we calculate the real part of the static Raman susceptibility $\chi^{XY}_{0}(T,x)$ for $B_{2g}$ symmetry. Figure. 3A shows $\chi^{XY}_{0}(T,x)$ in a $T$–$x$ phase diagram where $T_S(x)$, $T_{SDW}(x)$, and $T_c(x)$ obtained by transport measurements (23) are superimposed on top. The enhancement of $\chi^{XY}_{0}(T,x)$ with cooling, observed for all x, starts from high temperatures and culminates in a maximum at the structural transition $T_S(x)$ or at a smaller maximum before the $T_c(x)$—line for higher dopings. $\chi^{XY}_{0}(T,x)$ is suppressed below the structural transition $T_S(x)$.

The two sharp modes in $\chi''_{A_{1g}}$ at $\approx 164$ and $\approx 195$ cm$^{-1}$, and in $\chi''_{B_{1g}}$ at $\approx 211$ cm$^{-1}$ observed in the spectra for all dopings and temperatures are phonon excitations (Fig. 2GHI), as they are expected for the 111-family crystallographic structure (43). The frequencies of these phonons increase slightly with cooling, typical of anharmonic behavior, and do not display any anomalies in self-energy upon crossing phase transition lines.

For low dopings, the $\chi''_{A_{1g}}$ susceptibility displays an overall enhancement of the spectra upon transversing the high-temperature tetragonal phase to the orthorhombic and SDW phases which maximizes at lower temperatures. For $x \approx 0.0175$, the most important changes occur in the low-
frequency region below $\approx 200 \text{ cm}^{-1}$ when crossing from the normal into the superconducting state. Here $\chi_{Al}$ displays markedly different dynamics above and below $T_c(x)$, with featureless spectra above $T_c(x)$ and below, one or more superconducting features in the range of $\approx 70 \text{ cm}^{-1}$.

The $B_{2g}$ symmetry channel, $\chi''_{XY}(\omega)$ contains several characteristics: (i) a broad peak extending to about 400 cm$^{-1}$, indicated by green shading, which is dominating in the entire tetragonal phase above the $T_S(x)$ and $T_c(x)$ lines; (ii) a low-frequency suppression and coherence peak in the orthorhombic phase, indicated by light blue shading; (iii) a sharp resonance in the superconducting phase, indicated by blue shading; (iv) a broad continuum which diminishes with doping, indicated by blue shading (Fig. S7A); (v) a minor feature at $\approx 250 \text{ cm}^{-1}$ present at all temperatures which decreases with doping, indicated by magenta shading (Fig. S7A).

In the tetragonal phase, above the $T_S(x)$ and $T_c(x)$ lines, $\chi''_{XY}(\omega)$ can be decomposed into three components (Fig. S7A) which includes a continuum, a minor peak at $\approx 250 \text{ cm}^{-1}$ and a broad mode of relaxational shape.

Both the intensity of the continuum and of the $\approx 250 \text{ cm}^{-1}$ mode diminishes rapidly with doping, and vanishes near $x\approx 0.025$ (Fig. S7BD). They likely involve the $\beta$ band as its FS reduces with doping (See Fig. 1BD) with the continuum due to intraband excitations and the $\approx 250 \text{ cm}^{-1}$ mode due to $\alpha$-to-$\beta$ interband transitions. This finding is consistent with first-principle calculations taking into account spin-orbit coupling, Fig. 1C and fig. S5.

In the tetragonal phase above $T_S(x)$ and $T_c(x)$, $\chi''_{XY}(\omega, T, x)$ reveals the emergence of broad quasielastic scattering (QES) peaked at $\omega_P(T, x)$ (Figs. 4,5 and fig. S7). The intensity of this feature is weak at high temperatures. Upon cooling, it softens and gains in intensity, where it maximizes at the $T_S(x)$--line and near $T_c(x)$. The QES is suppressed abruptly below $T_S(x)$. Below $T_c(x)$ the intensity reappears as a sharp resonance at $\omega^h_{B_{2g}} \approx 57 \text{ cm}^{-1}$ (7.1 meV) which gains in strength upon cooling deeper into the superconducting state, Figs. 4F,5. It is remarkable that at base temperature the extraordinarily strength of this resonance is stronger than the phonon modes, Fig. 4F.

The shape of the broad peak can be described as a relaxational mode (RM), $\chi_{XY}^{RM}(\omega, T, x) \propto$
$A(x)[\omega_P(T, x) - i\omega]^{-1}$. The intensity of the RM decreases with doping (Fig. S7C). The frequency $\omega_P(T, x)$ decreases linearly upon cooling below $\approx 100$ K for all dopings, $\omega_P(T, x) \propto [T - T_0(x)]$, see insets to Figs. 4D-F,5. The linear extension crosses the temperature axis at $T_0(x)$. The decrease of $T_0(x)$ with doping can be described by a linear function $T_0(x) = b - ax$ which is zero at $x \approx 0.02$ and negative for $x \gtrsim 0.02$ (Fig. S7E). In the $T-x$ phase diagram, Fig. 3A, the $T_0(x)-$line is parallel to the $T_{SDW}(x)$ and $T_S(x)-$lines (44), approximately 10 and 20 K below, respectively, for $x \lesssim 0.02$.

The real part of the static Raman susceptibility $\chi_{XY}(T, x)$ increases upon cooling above $T_S(x)$ or $T_c(x)$ below which it rapidly falls off, Fig. 3B. The increase can be scaled to the universal response function $\chi_{XY}(T, x) \propto [T - T_0(x)]^{-1}$ for all doping concentrations $x$ with a linear temperature dependence of $T_0(x)$. The inset shows the inverse of $\chi_{XY}(T, x)$, which exhibits the same linear behavior with temperature as $\omega_P(T, x)$ of the RM.

The behavior of $\chi_{XY}(\omega, T, x)$ cannot be understood in a scenario of non-interacting incoherent quasiparticle excitations which would only produce a featureless low-frequency response in $\chi''_{XY}(\omega, T, x)$ (29). Thus, the $\chi_{XY}(\omega, T, x)$ susceptibility in the $B_{2g}$ symmetry channel exhibiting emergent critical behavior is a result of electronic interactions. In order to capture the collective behavior of the RM we use an expression for interacting susceptibilities,

$$\chi_{XY}(\omega, T, x) = \lambda^2 \frac{\chi_{XY}^{(0)}(\omega, T, x)}{1 - g\chi_{XY}^{(0)}(\omega, T, x)}.$$  \hspace{1cm} (2)

Here, $\lambda$ is the coupling of light to the quadrupole fluctuations in $XY$ symmetry (mainly to the $\gamma$ and $\beta$ bands (Fig. S6)) $\chi_{XY}^{(0)}(\omega, T, x)$ is the non-interacting susceptibility and $g$ is the coupling constant, describing the scattering processes shown in Fig. 7B. Our basic assumption of the attraction in the $d^{\pm}$ $p$-$h$ channel implies $g > 0$. The resulting critical behavior of the susceptibility $\chi_{XY}(\omega, T, x)$ manifests in the scaling of $\chi_{XY}^{(0)}(T, x)$ to $[T - T_0(x)]^{-1}$ upon cooling and the gain in intensity and near-linear slowdown of the characteristic fluctuation frequency $\omega_P(T, x) \propto T - T_0(x)$. The linear decrease of $T_0(x)$ is caused by progressive deviation from nesting with doping as illustrated in Fig. 1CD (45). For higher dopings, the electron and hole
FSs uncouple and our assumption of attraction in the $d^{\pm} p-h$ channel eventually breaks down. Hence, the criticality persists but weakens with doping. It is striking that $\omega_p(T, x)$ scales to the same $[T - T_0(x)]$ behavior as $\chi_{XY}^0(T, x)$, in which the former does not soften near $T_S(x)$, indicating that the critical slowdown is intervened abruptly at $T_S(x)$ approximately 20 K above $T_0(x)$.

The critical quadrupole fluctuations above $T_S(x)$ and $T_c(x)$ seek to establish a ground state at $T_0(x)$ in which the quadrupole lattice is ordered in a $\Gamma_4^+$ orbital pattern (Fig. S4A). The critical behavior of $\chi_{XY}(\omega, T, x)$ foretells the approaching second order phase transition which is destined to break $C_4-$symmetry, but without instigating a DW instability.

In the orthorhombic phase $\chi''_{XY}(\omega, T, x)$ is characterized by a low-frequency suppression of spectral weight which develops below $T_S(x)$. Simultaneously, a peak at $2\Delta_{DW}$ emerges upon cooling (Figs. 4ABDE). For $x=0$, $2\Delta_{DW}$ is at $\approx 300$ cm$^{-1}$ and decreases with doping. For $x \gtrsim 0.0175$, the low-frequency suppression and the peak are absent. The evolution with frequency and temperature in the low-doping regime is captured in the color contour plots shown in Figs. 4A-C.

We now consider the nature of the structural instability at $T_S(x)$ which intervenes the formation of the pursued $\Gamma_4^+$ quadrupole state described above (Fig. S3A). At the M-point in k-space, the quadrupole excitations are doubly degenerate with two possibilities of orbital stripe patterns along either the $x$ or $y$ direction (Fig. S3B) corresponding to $M_5^+-symmetry$. In either configuration, two neighboring stripes have opposite orbital occupation. An $M_5^+$ Fe-ion vibration (Fig. S3C) modulates the interaction commensurately between the stripes. The Jahn-Teller theorem predicts that such $M_5^+ \otimes M_5^+$ quadrupole—phonon interactions lead to a new ground state with lifted degeneracy (46). The new quadrupole ground state has rearranged orbitals in one of the striped patterns (Fig. S3D) which instigates a first order structural transition. This new ground state doubles the unit cell, breaks $C_4$ symmetry, and induces ordered charge modulations below $T_S(x)$ as a DW gap at $2\Delta_{DW}$ in $XY-$symmetry.

In the superconducting state, the Raman susceptibility contains features in both $A_{1g}$ and
Below $T_c(x)$, a resonance emerges in $B_{2g}$ symmetry which sharpens, gains in strength and hardens to $\omega_{B_{2g}} \simeq 7.1$ meV upon cooling for $x \gtrsim x_c$, Figs. 4F, 5, 6. It is the strongest near $x_c$ at $x=0.0175$, and then decreases in strength for increasing doping still prevailing for $x=0.05$ and vanishes for $x=0.08$. The doping dependence of the superconducting features at 5 K in both $\chi''_{A_1g}(\omega)$ (top row) and $\chi''_{XY}(\omega)$ (bottom row) in comparison to normal state spectra at 23 K is summarized in Fig. 6. In the top panel, $\omega_{A_{1g}} \simeq 68$ cm$^{-1}$ (8.5 meV), $2\Delta_\gamma$ and $2\Delta_{\epsilon\delta}$ are present from $x=0.0175$ to $x=0.05$, and are nearly independent of doping (Fig. S4A). $2\Delta_\gamma$ and $2\Delta_{\epsilon\delta}$ are consistent with ARPES (26, 47) and are assigned as pair-breaking excitations across the corresponding superconducting gaps (Fig. 6). The width of $\omega_{B_{2g}}$ remains at less than 1 meV from $x=0.0175$ to $x=0.0225$ (Fig. S4B) whereafter it broadens and its intensity diminishes gradually until it vanishes before $x=0.08$. $\omega_{B_{2g}} \simeq 25$ cm$^{-1}$ (3.1 meV) appears at the boundary of the DW phase ($x=0.0175$) and becomes stronger for decreasing doping while $\omega_{B_{2g}}$ weakens (Fig. 7A and fig. S4C). All of $\omega_{A_{1g}}$, $\omega_{B_{2g}}$ and $\omega_{B_{2g}}$ qualify as true ingap excitations as their energy lies below the minimal quasiparticle gap, $2\Delta_\gamma$, Fig. 6. For lower dopings, no superconducting features are observed (Fig. 6 and fig. S4C).

Next we interpret the spectrum of collective modes, Fig. 7A. We assign $\omega_{A_{1g}}$ to a $p-h$ charge exciton as suggested in Ref. (31, 41). The significant intensity of the $\omega_{B_{2g}}$ mode suggests that it couples to light directly, implying that it is the $d$-wave counterpart of the $\omega_{A_{1g}}$ exciton. Because $\chi_{XY}(\omega, T, x)$ is controlled by a large coupling constant, $g$ (eq. (2)), the $\omega_{B_{2g}}$ resonance, which is facilitated by the positive feedback of the superconductivity, emerges from the RM upon cooling through $T_c$ while retaining its identity as a bound state of $d^\pm p-h$ plasma oscillations.

To elucidate this mechanism, we argue that the $\omega_{B_{2g}}$ exciton promotes $s^\pm$ pairing. The latter is stabilized if the inter-pocket repulsion exceeds the intra-pocket interaction. Therefore, the optimal situation is reached when the exciton mediated attraction neutralizes the intra-pocket repulsion (3). Such an attraction is operational at energies below $\omega_{B_{2g}}$ and is similar to the attraction in the BCS model. The superconducting gap in turn removes low-lying excitations, promoting the coherence of the $\omega_{B_{2g}}$ exciton and pulls it up in energy with more electrons.
benefitting from the attraction. As a result, the $\omega^{p-h}_{B_{2g}}$ exciton acts as a mediator for the $s^\pm$ Cooper pairing and is itself affected by the superconductivity.

The same argument when applied to a symmetric $p-h$ channel shows how the strong $\omega^{p-h}_{B_{2g}}$ exciton assists $\omega^{p-h}_{A_{1g}}$. Indeed, suppression of intra-pocket repulsion stabilizes $\omega^{p-h}_{A_{1g}}$ in the same way as it stabilizes the $s^\pm$ pairing. Thus our main assumption of a large $d^\pm$-wave coupling constant $g$ yields the RM above $T_c$, the $s^\pm$ superconductivity, and both $\omega^{p-h}_{B_{2g}}$ and $\omega^{p-h}_{A_{1g}}$ below $T_c$.

The much weaker $B_{2g}$ feature, $\omega^{p-p}_{B_{2g}}$ exists only in a narrow doping window of DW and superconductivity coexistence (12, 26) which we attribute to a Bardasis-Schrieffer exciton, Fig. 7A. In the coexistence region, $s$- and $d$-wave channels couple resulting in attraction induced in the $d$-wave channel. As a result, the ingap $d$-wave Cooper pair exciton, $\omega^{p-p}_{B_{2g}}$ forms. As the energy of the $\omega^{p-p}_{B_{2g}}$ exciton softens at the transition to the coexistence region it decouples from $\omega^{p-h}_{B_{2g}}$ (37, 38). This allows $\omega^{p-p}_{B_{2g}}$ to survive as a distinct excitation by borrowing spectral intensity from $\omega^{p-h}_{B_{2g}}$.

Our study of NaFe$_{1-x}$Co$_x$As reveals a number of phenomena giving rise to new insights into superconductivity in iron pnictides. The results point to a common origin of the normal state near-critical dynamics and superconductivity. We find that the tetragonal phase is dominated by non-symmetric interband collective excitations possible only in multiband materials. These are the correlated plasma waves of quadrupole excitations. In the normal state, these plasmons exhibit critical slowdown which are intervened by the structural transition at low dopings and by superconductivity at higher dopings. Below $T_c$, the near-critical plasmons undergo a metamorphosis into an anomalously sharp and strong particle-hole exciton modes carrying most of the spectral weight. This transformation is due to the positive feedback of the exciton to the superconductivity. We hence present a consistent picture of superconductivity in its relation to the normal state properties valid across the entire phase diagram. These findings elucidate the origin of superconductivity in NaFe$_{1-x}$Co$_x$As, and being of general character, have relevance to the whole family of iron pnictides.
References and Notes

1. J. Paglione, R. L. Greene, *Nat. Phys.* **6**, 645 (2010).

2. F. Wang, D.-H. Lee, *Science* **332**, 200 (2011).

3. A. Chubukov, *Annual Review of Condensed Matter Physics* **3**, 57 (2012).

4. J. Zhao, *et al.*, *Nature Mater.* **7**, 953 (2008).

5. S. Li, *et al.*, *Phys. Rev. B* **79**, 174527 (2009).

6. L. Ma, *et al.*, *Phys. Rev. B* **83**, 132501 (2011).

7. X. Lu, *et al.*, *Science* **345**, 657 (2014).

8. S. Oh, *et al.*, *Phys. Rev. B* **88**, 134518 (2013).

9. Y. Nakai, *et al.*, *Phys. Rev. Lett.* **105**, 107003 (2010).

10. F. L. Ning, *et al.*, *Phys. Rev. Lett.* **104**, 037001 (2010).

11. G. F. Ji, *et al.*, *Phys. Rev. Lett.* **111**, 107004 (2013).

12. S. Oh, *et al.*, *Phys. Rev. B* **87**, 174517 (2013).

13. C. Zhang, *et al.*, *Phys. Rev. B* **88**, 064504 (2013).

14. I. I. Mazin, D. J. Singh, M. D. Johannes, M. H. Du, *Phys. Rev. Lett.* **101**, 057003 (2008).

15. H. Kontani, S. Onari, *Phys. Rev. Lett.* **104**, 157001 (2010).

16. Z. P. Yin, K. Haule, G. Kotliar, *Nature Phys.* (2014).

17. T. T. Ong, P. Coleman, *Phys. Rev. Lett.* **111**, 217003 (2013).

18. S. Hanaguri, S. Niitaka, K. Kuroki, H. Takagi, *Science* **328**, 474 (2010).
19. M. D. Lumsden, \textit{Phys. Rev. Lett.} \textbf{102} (2009).

20. M. A. Tanatar, \textit{et al.}, \textit{Phys. Rev. Lett.} \textbf{104}, 067002 (2010).

21. J.-P. Reid, \textit{et al.}, \textit{Superconductor Science and Technology} \textbf{25}, 084013 (2012).

22. M. Yamashita, \textit{et al.}, \textit{Phys. Rev. B} \textbf{84}, 060507 (2011).

23. G. Tan, \textit{et al.}, \textit{Phys. Rev. B} \textbf{87}, 144512 (2013).

24. Y. Zhang, \textit{et al.}, \textit{Phys. Rev. B} \textbf{85}, 085121 (2012).

25. M. Yi, \textit{et al.}, \textit{New Journal of Physics} \textbf{14}, 073019 (2012).

26. Q. Q. Ge, \textit{et al.}, \textit{Phys. Rev. X} \textbf{3}, 011020 (2013).

27. J.-H. Chu, H.-H. Kuo, J. G. Analytis, I. R. Fisher, \textit{Science} \textbf{337}, 710 (2012).

28. S. Kasahara, \textit{et al.}, \textit{Nature} \textbf{486}, 382 (2012).

29. M. V. Klein, S. B. Dierker, \textit{Phys. Rev. B} \textbf{29}, 4976 (1984).

30. M. V. Klein, \textit{Phys. Rev. B} \textbf{82}, 014507 (2010).

31. M. V. Klein, \textit{Physics} \textbf{2}, 46 (2009).

32. T. P. Devereaux, R. Hackl, \textit{Rev. Mod. Phys.} \textbf{79}, 175 (2007).

33. C. Sauer, G. Blumberg, \textit{Phys. Rev. B} \textbf{82}, 014525 (2010).

34. I. I. Mazin, \textit{et al.}, \textit{Phys. Rev. B} \textbf{82}, 180502 (2010).

35. P. M. Platzman, \textit{Phys. Rev.} \textbf{139}, A379 (1965).

36. H. Monien, A. Zawadowski, \textit{Phys. Rev. B} \textbf{41}, 8798 (1990).

37. A. Bardasis, J. R. Schrieffer, \textit{Phys. Rev.} \textbf{121}, 1050 (1961).
38. M. Khodas, A. V. Chubukov, G. Blumberg, *Phys. Rev. B* **89**, 245134 (2014).

39. A. J. Leggett, *Progress of Theoretical Physics* **36**, 901 (1966).

40. G. Blumberg, *et al.*, *Phys. Rev. Lett.* **99**, 227002 (2007).

41. A. V. Chubukov, I. Eremin, M. M. Korshunov, *Phys. Rev. B* **79**, 220501 (2009).

42. L. N. Ovander, *Optics and Spectroscopy* **9**, 302 (1960).

43. Y. J. Um, *et al.*, *Phys. Rev. B* **85**, 012501 (2012).

44. NaFe$_{1-x}$Co$_x$As has in contrast to most other pnictides $T_S(x)$ and $T_{SDW}(x)$ separated by $\simeq 10$ K.

45. I. Paul, *Phys. Rev. B* **90**, 115102 (2014).

46. I. B. Bersuker, *Chem. Rev.* **101**, 1067 (2001).

47. Z.-H. Liu, *et al.*, *Phys. Rev. B* **84**, 064519 (2011).

48. **Acknowledgments** We thank P. Coleman, R. M. Fernandes, Y. Gallais, K. Haule, T. T. Ong, A. Sacuto, and W.-L. Zhang for discussions. We thank A. Ignatov and A. Lee for assisting with the measurements. The crystal growth efforts at UTK and Rice were supported by the US DOE, BES, through contract DE-FG02-05ER46202. M.K. thanks the University of Iowa for support. V.K.T. acknowledges support from NSF through Award DMR-1104884. Research at Rutgers was supported support by the US Department of Energy, Office of Basic Energy Sciences through Award DE-SC0005463.
Figure 1: NaFe$_{1-x}$Co$_x$As crystal and electronic structure, and $XY-q$ quadrupole mode. (A) Crystal structure of NaFeAs in the tetragonal phase. (B) Top view of FeAs layer in the tetragonal phase shown with $d_{xz}-d_{yz}$ orbitals (left) and $d_{xy}$ orbitals (right). Dashed lines represent the two/four-Fe unit cell in the tetragonal/orthorhombic phase. (C and D) The effect of Co-doping is illustrated on the schematic Fermi surfaces (FS) for NaFe$_{1-x}$Co$_x$As in the tetragonal nonmagnetic BZ for doping $x=0$ (C) and $x>0$ (D). Below is shown a band-dispersion cut along the $\Gamma-M$ high-symmetry line. $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals are shown with respectively red, blue and green colors. The hole-like pockets $\alpha$, $\beta$ and $\gamma$ surround the $\Gamma$ point, and the electron-like pockets $\epsilon/\delta$ surround the M point. (E) Momentum- and frequency-resolved spectra $A(k,\omega)$ along the $\Gamma-M$ high-symmetry line calculated by first-principle calculations including spin-orbit coupling (SOM). (F) Neutral quadrupole charge density modulation in the $B_{2g}$ symmetry channel. The mode is sustained by charge transfers involving $d_{xz}-d_{yz}$ Fe-orbitals. (G) Phase of the superconducting OPs for the $\gamma$ band at the $\Gamma$-point and the $\delta/\epsilon$ bands at the M-point for $s^{++}$, $d^{++}$, $s^{\pm}$, and $d^{\pm}$ symmetry. Different colors indicate opposite phase.
Figure 2: **Raman susceptibility $\chi''(\omega)$ in the $A_{1g}$, $B_{2g}$ and $B_{1g}$ symmetry channels at representative temperature and dopings.** (A to C) $\chi''_{A_{1g}}(\omega)$ showing superconducting features highlighted with blue shading below $\sim 200$ cm$^{-1}$ ($x=0.0175$, $x=0.05$). (D to F) $\chi''_{B_{2g}}(\omega)$ presenting a quasielastic scattering relaxational mode above $T_S(x)$ and $T_c(x)$ highlighted with green shading, a density wave suppression and coherence peak highlighted with light blue shading below $T_S(x)$ ($x=0$, 5 K), and a low-temperature collective resonance highlighted with blue shading ($x=0.0175$, $x=0.05$, 5 K). (G to I) $\chi''_{B_{1g}}(\omega)$ featuring mainly a $B_{1g}$ phonon.
Figure 3: Static Raman susceptibility $\chi_0^{XY}(T, x)$ in the $B_{2g}$ symmetry channel. (A) Evolution of $\chi_0^{XY}(T, x) = 2/\pi \int_0^\infty (\chi''_{XY}(\omega)/\omega) d\omega$ as a function of temperature and doping. The structural transition $T_S(x)$, the magnetic transition $T_{SDW}(x)$, and the superconducting transition temperature $T_c(x)$ (from Ref. (23)) are indicated by blue triangles, purple squares and red circles respectively. $T_0(x)$ is the mean field transition temperature associated with the critical behavior of $\chi_0^{XY}(T, x)$. (B) $\chi_0^{XY}(T, x)$ is shown with a universal fit to $A/(T - T_0(x))$ where the temperature axis for each doping $x$ is shifted by $T_0(x)$. The inset shows the inverse of $\chi_0^{XY}(T, x)$ versus temperature $T - T_0(x)$ with a fit to a universal straight line.
Figure 4: **Raman susceptibility** $\chi''_{XY}(\omega, T)$ in the $B_{2g}$ symmetry channel at dopings $0 \leq x \leq 0.0175$. (A to C) Temperature and frequency evolution of $\log(\chi''_{XY}(\omega, T))$ at dopings $x=0$, $x=0.015$ and $x=0.0175$. The structural transition $T_S(x)$ is indicated on the temperature axis, and the coherence peak, $2\Delta_{DW}$ on the frequency axis for $x=0$ and $x=0.015$. (D to F) $\chi''_{XY}(\omega)$ for $T \leq 100$ K displaced vertically for clarity. All dopings show the development of the relaxational mode (RM) in the tetragonal phase described by, $A(x) [\omega_P(T, x) - i\omega]^{-1}$; $x=0$ and $x=0.015$ show the development of the coherence peak and spectral weight suppression in the orthorhombic phase; $x=0.0175$ show the emergence of the sharp resonance in the superconducting phase. The insets display $\omega_P(T, x)$ versus temperature.
Figure 5: Raman susceptibility $\chi''_{XY}(\omega, T)$ in the $B_{2g}$ symmetry channel at dopings $0.02 \leq x \leq 0.08$. (A to E) $\chi''_{XY}(\omega, T)$ at various temperatures displaced vertically for clarity. All dopings show the development of the relaxational mode (RM) in the tetragonal phase described by, $A(x)[\omega_P(T, x) - i\omega]^{-1}$ and the emergence of the sharp resonance in the superconducting phase.
Figure 6: **Raman susceptibilities** $\chi''_{XX}(\omega) - \chi''_{xy}(\omega)$ and $\chi''_{XY}(\omega)$ in the superconducting state. $\chi''_{XX}(\omega) - \chi''_{xy}(\omega)$ (top row) and $\chi''_{XY}(\omega)$ (bottom row) in the superconducting (5 K) and normal (23 K) states at doping levels as indicated. The vertical dashed line, shown for $x=0.0175$ and $x=0.05$ indicates the lowest superconducting gap determined by ARPES at respectively $\simeq 9$ meV (26) and $\simeq 10$ meV (47).
Figure 7: **Energy diagram in the superconducting state.** (A) Energy diagram showing the superconducting condensate, the superconducting gap and the ingap collective modes $\omega_{A_{1g}}^{p-h}$ and $\omega_{B_{2g}}^{p-h}$ are shown together with their spectroscopic signatures in the Raman data. The data was obtained with an excitation energy of $\omega_L = 2.6$ eV, except for the two lighter blue data containing $\omega_{B_{2g}}^{p-p}$ where $\omega_L = 1.91$ eV was used. The former is close to resonance condition while the latter is pre-resonant which changes the couplings to the modes in the $p-h$ and $p-p$ channels. (B) The ingap collective modes, $\omega_{A_{1g}}^{p-h}$ and $\omega_{B_{2g}}^{p-h}$ originate from the $p-h$ channel giving rise to a quadrupole mode in the BZ illustrated respectively to the left and right. (See SOM). $\omega_{B_{2g}}^{p-p}$ originates from the $p-p$ channel.