

Ultrafast Pump-Probe Study of Phase Separation and Competing Orders in the Underdoped (Ba, K)Fe₂As₂ Superconductor

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We report measurements of quasiparticle relaxation dynamics in the high-temperature superconductor (Ba, K)Fe₂As₂ in optimally doped, underdoped, and undoped regimes. In the underdoped sample, spin-density wave (SDW) order forms at ~ 85 K, followed by superconductivity at ~ 28 K. We find the emergence of a normal-state order that suppresses SDW at a temperature $T^* \sim 60$ K and argue that this normal-state order is a precursor to superconductivity.

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The recently discovered FeAs-based pnictides [1–5] constitute the only class of superconductors (SCs), besides the cuprates, with superconducting transition temperatures (T_c) exceeding 50 K. The pnictides have a layered structure like the cuprates, with FeAs planes instead of CuO₂ planes. Like many other SCs on the border of magnetism, such as the organics [6], heavy-fermions [7], and cuprate high-temperature superconductors (HTSCs) [8–10], the pnictides exhibit a rich phase diagram, with antiferromagnetism (or spin-density wave, SDW) at low dopings [11] and SC at intermediate dopings. Figure 1(a) shows the phase diagram of a particular family of pnictides—(Ba, K)Fe₂As₂ (BKFA) [12], which is the subject of study in this Letter. These phases in BKFA are mesoscopically separated in the underdoped compound, with SDW and SC-normal-state regions [13]. Moreover, inelastic neutron scattering in an optimally doped BKFA revealed the presence of a 14 meV magnetic resonance mode in the SC phase, localized in both energy and wave vector [14]. A large Fe-isotope effect was seen in BKFA, suggesting the role played by magnetic fluctuations in superconductivity [15]. In all these classes of SCs, how these phases interact with one another, and the role of magnetism, are open questions that might help understand superconductivity in these compounds.

In the cuprate HTSCs, femtosecond pump-probe spectroscopy has shown to be a useful tool to discern coexisting or competing phases, such as the pseudogap phase in YBa₂Cu₃O_{7-x} (Y-123) [16], and the suppression of superconductivity by antiferromagnetism in the tri-layered Tl₂Ba₂Ca₂Cu₃O_y [17]. In this Letter, we use the pump-probe technique to study the BKFA SCs in the undoped, underdoped and optimally doped regimes. In the underdoped sample, we observed the existence of three energy scales—SDW (at Néel temperature $T_N \sim 85$ K), supercon-

ductivity (at $T_c \sim 28$ K) and a normal-state phase (at $T^* \sim 60$ K). We observed the smooth evolution of this normal-state phase into the SC phase, and the suppression of SDW by this normal-state phase. We attribute this normal-state phase to the emergence of precursor superconductivity. We incorporated the existing ideas of phase separation and magnetic resonance mode, and introduced new ideas of spin susceptibility renormalization, emergence of precursor order, and the competition between SDW and superconductivity.

Single-crystalline BKFA samples with sizes up to 10 mm \times 5 mm \times 0.5 mm were grown by high-temperature solution method [18]. The grown crystals were cleaved to reveal a fresh surface for our measurements. The values of T_c were confirmed by magnetization data using a Quantum Design Magnetic Property Measurement System. No hysteresis loops in magnetization versus field were found, ruling out the presence of ferromagnetic impurities. The pump-probe setup was described in Ref. [17], where cross-polarized, 800 nm pump and probe pulses, with 40 fs pulse width and 80 MHz repetition rate, were used. The average pump power was 1–2 mW, giving a pump fluence of $\sim 0.2 \mu\text{J}/\text{cm}^2$. The probe intensity was 10 times lower. Data, corrected for temperature increase of the illuminated spot, were taken from 8 to 140 K. The resolution is at least 1 part in 10^6 .

Figure 1(b) shows the photoinduced change in reflectance ($\Delta R/R$) of the almost optimally-doped sample (OPT), $T_c \sim 36$ K, as a function of temperature. When the pump pulse arrives, the reflectance drops sharply and then recovers its undisturbed value on a picosecond (ps) time scale. We notice a very fast initial relaxation, that is temperature-independent, of the order of the pulse width, which we attribute to the appearance of the coherent

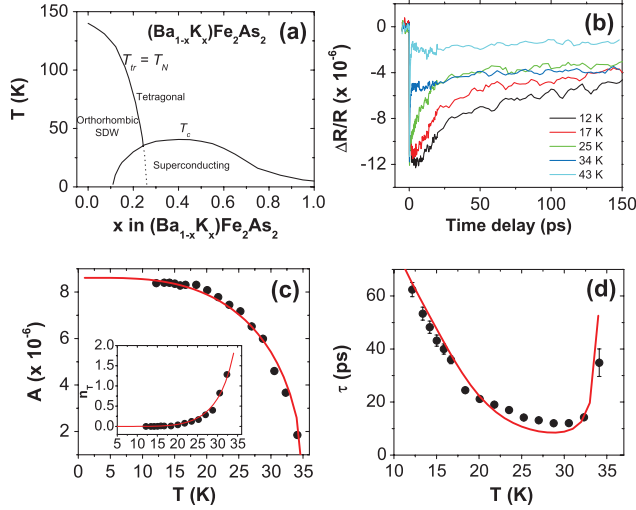


FIG. 1 (color). (a) Phase diagram of BKFA, with T_c and structural phase transition temperature (T_{tr}) (adapted from [12]). T_N coincides with T_{tr} until both are suppressed [39]. (b) $\Delta R/R$ versus pump-probe delay of optimally doped BKFA ($T_c \sim 36$ K). (c) Amplitude A extracted from single-exponential decay fits. Inset: Density of thermally-excited QPs, $n_T(T)$. Solid lines are fits to the RT model, yielding $\Delta(0) = 3.0k_B T_c$. (d) Relaxation time $\tau(T)$. Solid line is the fit to the RT model.

artifact. We will ignore it in our subsequent analysis. After the decay of the artifact, the photoinduced change in reflectance can be described by a single-exponential decay function when the statistical transfer of energy from quasiparticles (QP) to the thermal reservoir is dominated by a single relaxation channel. We extract the amplitude (A) and relaxation time (τ) of $\Delta R/R$ by fitting it with a single-exponential decay function, $\Delta R/R = A \exp(-t/\tau)$. The fitting parameters $A(T)$ and $\tau(T)$ in the SC state are shown in Figs. 1(c) and 1(d).

We use the Rothwarf-Taylor (RT) model to explain our data [19]. This phenomenological model is used to describe the relaxation of photoexcited SCs, where the presence of a gap in the QP density of states (DOS) gives rise to a bottleneck for carrier relaxation. When two QPs with energies $\geq \Delta$ recombine ($\Delta =$ SC gap magnitude), a high-frequency boson (HFB) with energy $\omega \geq 2\Delta$ is created. The HFBs that remain in the excitation volume can subsequently break additional Cooper pairs effectively inhibiting QP recombination. Superconductivity recovery is governed by the decay of the HFB population. From the temperature-dependence of the amplitude A , one obtains the density of thermally excited QPs n_T via $n_T \propto [A(T)/A(T \rightarrow 0)]^{-1} - 1$. Then we fit the n_T data to the QP density per unit cell $n_T \propto \sqrt{\Delta(T)T} \exp(-\Delta(T)/T)$, with $\Delta(0)$ as a fitting parameter. Moreover, for a constant pump intensity, the temperature dependence of n_T also governs the temperature dependence of the relaxation time τ , given by

$$\tau^{-1}(T) = \Gamma[\delta + 2n_T(T)][\Delta(T) + \alpha T \Delta(T)^4], \quad (1)$$

where Γ , δ and α are fitting parameters, with α having an upper limit of $52/(\theta_B^3 T_{\min})$, θ_B being the temperature of the characteristic boson, and T_{\min} the minimum temperature of the experiment [20–22].

Figure 1(c) shows $A(T)$ and the corresponding $n_T(T)$ in its inset. Assuming that $\Delta(T)$ obeys a BCS temperature dependence, our fits to $A(T)$ and $n_T(T)$ yield $\Delta(0) = 3.0k_B T_c$, agreeing with the value obtained from photoemission data [23]. We also fit $\tau(T)$ [Fig. 1(d)] using Eq. (1). The good fit shows that the QP relaxation dynamics in the OPT compound is well described by the presence of a gap in the DOS at the Fermi level.

We now focus on underdoped BKFA ($T_c \sim 28$ K) and demonstrate that this compound exhibits a *competition* between the SC and SDW orders. The suppression of SDW order starts at $T^* \sim 60$ K, far above T_c . Our subsequent analysis suggests that the Cooper pairs might preform above T_c , though without phase coherence.

Figure 2 shows $\Delta R/R$ of underdoped BKFA at different temperatures [24]. We observe three relaxation processes below T_c , two between T_c and T^* , and one between T^* and T_N . A three-exponential decay in the SC state was also seen in pump-probe data of Sm(O,F)FeAs single crystals [25]. The slow component ($\tau_{\text{slow}} \sim 5\text{--}30$ ps) corresponds to QP recombination across the SC gap, as shown by the BCS-like temperature dependence of A_{slow} below T_c [Fig. 3(a)] and by the peak in τ_{slow} at T_c [Fig. 3(b)]. The identical RT analysis as for the OPT sample described above yields $\Delta(0) = 3.0k_B T_c$ [solid lines in Figs. 3(a) and 3(b)]. This shows that the opening of the SC gap in the underdoped sample governs the QP recombination by introducing a relaxation bottleneck.

Next, the fast relaxation component ($\tau_{\text{fast}} \lesssim 1$ ps) below $T_N \sim 85$ K bears the signatures of QP relaxation across the SDW gap: the relaxation time τ_{fast} displays a quasidivergence at T_N [Fig. 3(d)]. The appearance of SDW order in underdoped BKFA, and its coexistence with superconductivity, has also been reported in a muon spin rotation study [26]. The values of T_c and T_N in our underdoped sample and that of Ref. [26] are consistent with the phase diagram in Fig. 1(a). Our measurements not only confirm the coexistence of these two order parameters (evidenced by the existence of both the fast and the slow relaxations below T_c), but also uncover *competition* between SDW and superconductivity, as evidenced by the strong suppression of the SDW amplitude (A_{fast}) below T_c [Fig. 3(c)]. The close proximity of the SC and SDW regions in underdoped BKFA results in coupling between the SC and SDW order parameters, and causes the latter to be suppressed in the SC state [24]. The suppression of the SDW order parameter in the SC state was also observed in neutron diffraction data of the electron-doped Fe pnictide $\text{Ba}(\text{Fe}, \text{Co})_2\text{As}_2$ [27].

The sensitivity of the pump-probe technique to the presence of SDW order is further reinforced by our study of QP relaxation in the parent compound BaFe_2As_2 [24], with a simultaneous SDW and first-order structural phase

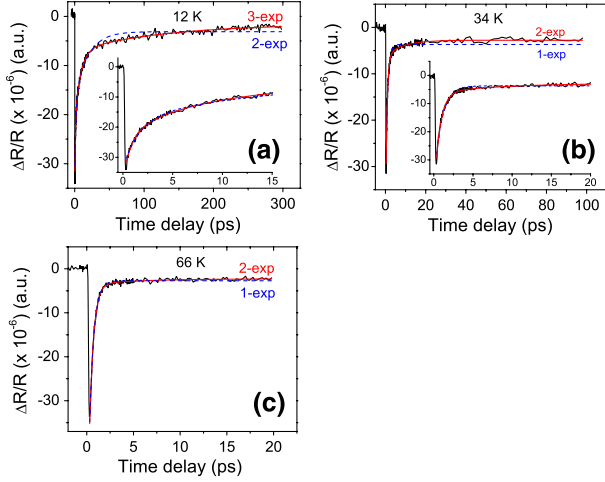


FIG. 2 (color online). $\Delta R/R$ in underdoped BKFA, $T_c \sim 28$ K. (a) 12 K, (b) 34 K, (c) 66 K. The solid and dashed lines are fits to single (1-exp), double (2-exp), or triple (3-exp), exponentials.

transition at $T_N \sim 130$ K [5]. Below T_N , the relaxation amplitude follows a BCS-like temperature dependence down to the lowest temperatures, reflecting the behavior of the SDW order parameter. In the vicinity of T_N , we see a quasidivergence in the relaxation time, which is the signature of a gap opening in the DOS at the Fermi level. This, together with our previous work on the itinerant antiferromagnet UNiGa₅ [22], shows that our technique is sensitive to SDW order. Data from the parent compound thus justify our attribution of the fast relaxation in underdoped BKFA below 85 K [Fig. 3(d)] to the SDW phase, and that the suppression of A_{fast} below T_c [Fig. 3(c)] corresponds to the suppression of the SDW order parameter.

Lastly, the slowest component ($\tau_{\text{slower}} \sim 100$ ps) [Fig. 3(f)] is largely temperature independent, disappears above T_c , and corresponds to spin-lattice relaxation. After the initial fast QP relaxation due to electron-phonon coupling (as manifested by τ_{fast}) in the SDW region, the heated phonons then relax by transferring their energy to the spin bath. This relaxation rate $1/\tau_{\text{sl}} = g_{\text{sl}}/C_{\text{spin}}$, where τ_{sl} is the spin-lattice relaxation time, g_{sl} is the spin-lattice coupling strength and C_{spin} is the spin specific heat [28]. Below T_c , the 14 meV magnetic resonance mode appears [14] in the SC region. This mode penetrates into the neighboring SDW regions and renormalizes the imaginary part of the dynamical spin susceptibility $\text{Im}\chi(\epsilon)$. The spin DOS in the SDW regions is given by $N_s(\epsilon) = -(1/\pi)\text{Im}\chi(\epsilon)$. In the SDW regions, above T_c , there is no renormalization of SDW fluctuations; hence, $N_s(\epsilon)$ at low energies is finite. Below T_c , the increase in amplitude of $\text{Im}\chi(\epsilon)$ at the resonance energy removes spectral weight at lower energies, resulting in the depression of $N_s(\epsilon)$ at low energies. Hence C_{spin} decreases, shortening τ_{sl} ($= \tau_{\text{slower}}$) to a value that is observable by our technique [24]. This scenario also explains why we do not observe τ_{slower} in the OPT sample—there are no SDW regions to begin with, hence no

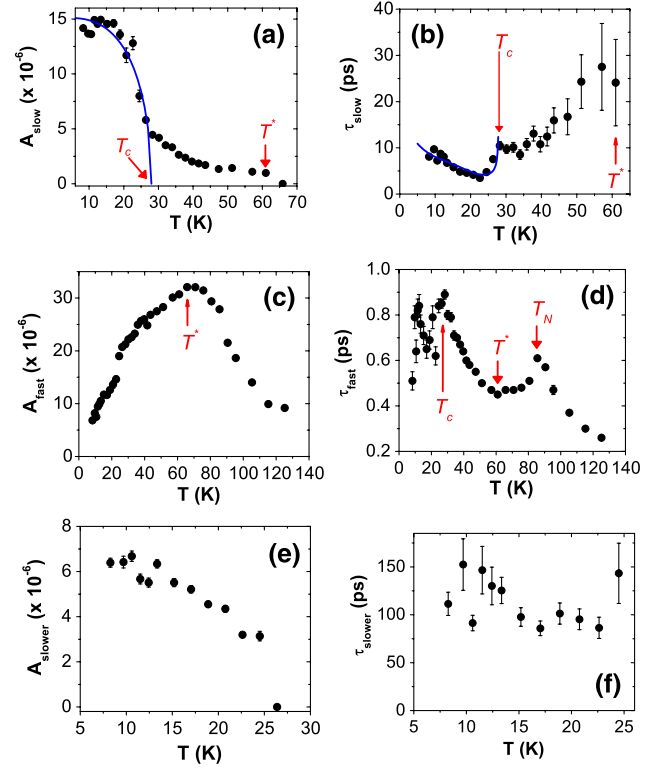


FIG. 3 (color online). For underdoped BKFA ($T_c \sim 28$ K), values of (a) A_{slow} , (b) τ_{slow} , (c) A_{fast} , (d) τ_{fast} , (e) A_{slower} , (f) τ_{slower} , as a function of temperature, extracted from $\Delta R/R$. In (a), beyond T^* , the slow component disappears. The solid lines in (a) and (b) are fits using the RT model. Near $T^* \sim 60$ K, we obtain large error bars in τ_{slow} because the one- and two-exponential fits of $\Delta R/R$ are of comparable quality.

SDW fluctuations for the magnetic resonance mode to renormalize.

In addition to establishing the competition between SDW and superconductivity, the data in Figs. 3(a)–3(d) carry evidence of a *precursor order* (PO) that appears at $T^* \sim 60$ K in the normal state of underdoped BKFA. In Fig. 3(a), A_{slow} exhibits a well-defined tail that survives well above T_c , and disappears above T^* . Compare this to A_{slow} of the OPT sample [Fig. 1(c)], where no such tail exists. This suggests that a kind of precursor superconductivity has already existed between T_c and T^* . A tail in the relaxation amplitude, attributed to the pseudogap, was also seen in underdoped Y-123 [16]. Moreover, in addition to a quasidivergence of τ_{slow} at T_c [Fig. 3(b)], indicative of the opening up of a SC gap, τ_{slow} continues to increase above T_c and peaks at T^* , showing that, at T^* , another QP gap opens up at the Fermi level. Compare this to a typical SC, where τ_{slow} plunges to the metallic value of ~ 0.5 ps immediately after T_c , and remains almost temperature-independent above T_c . We have also taken data on another underdoped BKFA with a similar T_c , and obtained a similar T^* of 55 K.

Further evidence for precursor pairing at T^* comes from the temperature dependence of A_{fast} —the SDW amplitude.

In the cuprate HTSCs, the proximity of d -wave superconductivity to antiferromagnetism is simply assumed as an experimental fact. However, from a microscopic point of view, d -wave superconductivity turns out to be the winner of the competition between these two orders [29]—this statement may also hold for the extended s_{\pm} pairing that the pnictide SCs are thought to have, where the gaps at the hole and electron pockets are of *opposite* signs to each other [30]. In our underdoped sample, if a PO develops at T^* , the SC fluctuations associated with the PO will start to “win over”, i.e., suppress, SDW even in the normal state. This would explain the suppression of SDW below T^* in our underdoped sample [Fig. 3(c)]. The rather broad peak in τ_{slow} at T^* might indicate the presence of disorder. It implies that, though the PO develops at T^* , disorder may cause the QP excitations to be partially gapless.

Due to partial Fermi surface nesting, the formation of SDW only induces a partial gap opening on the Fermi surface [31]. Thus, in the SDW islands, the fast relaxation rate is the sum of QP relaxations across the gapped and ungapped regions of the SDW Fermi surface: $1/\tau_{\text{fast}} = 1/\tau_{\text{fast}}^{\text{gapped}} + 1/\tau_{\text{fast}}^{\text{gapless}}$. Below T_c , the rise of the magnetic resonance mode in the neighboring SC regions renormalizes the SDW fluctuations in the SDW islands, making $\tau_{\text{fast}}^{\text{gapless}}$, and hence τ_{fast} , smaller than the corresponding τ_{fast} in the normal state. This explains the downturn of τ_{fast} in the SC state.

Recent photoemission data offered evidence of precursor pairing in the iron pnictide SCs, such as in La(O,F)FeAs [32,33] and Sm(O,F)FeAs [34]. The Nernst effect in La(O,F)FeAs also suggested the presence of a “precursor state” between T_c and 50 K in which magnetic fluctuations are strongly suppressed [35]. A recent pump-probe study of Sm(O,F)FeAs gave evidence of a pseudogaplike feature with an onset around 200 K [25]. In our case, the PO is associated with an intermediate energy scale T^* between magnetism and superconductivity. Our PO does not compete with superconductivity, but competes with the SDW order. The PO that sets in at T^* seems to be intimately related to superconductivity, as its signature becomes the signature of superconductivity below T_c . Therefore, we suggest that the PO may be a precursor of the SC order, much like the Cooper pairing without phase coherence that precedes macroscopic superconductivity in cuprate HTSCs. The detailed nature of the PO, whether it is due to phase fluctuations [29] or their interplay with disorder, remains an open scientific question. The ratio $T^*/T_c > 2$ has also been observed in underdoped cuprates [36], and various theories [37,38] have attempted to account for it.

In conclusion, our results on underdoped (Ba, K)Fe₂As₂ suggest the existence of precursor superconductivity above T_c that suppresses antiferromagnetism. We also offer evidence of the renormalization of SDW fluctuations by the magnetic resonance mode, in the framework of mesoscopic phase separation and partial SDW Fermi surface nesting.

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