Quantum Phase transition under pressure in a heavily hydrogen-doped iron-based superconductor LaFeAsO

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Hydrogen (H)-doped LaFeAsO is a prototypical iron-based superconductor. However, its phase diagram extends beyond the standard framework, where a superconducting (SC) phase follows an antiferromagnetic (AF) phase upon carrier doping; instead, the SC phase is sandwiched between two AF phases appearing in lightly and heavily H-doped regimes. We performed nuclear magnetic resonance (NMR) measurements under pressure, focusing on the second AF phase in the heavily H-doped regime. The second AF phase is strongly suppressed when a pressure of 3.0 GPa is applied, and apparently shifts to a highly H-doped regime, thereby a "bare" quantum critical point (QCP) emerges. A quantum critical regime emerges in a paramagnetic state near the QCP, however, the influence of the AF critical fluctuations to the SC phase is limited in the narrow doping regime near the QCP. The optimal SC condition \((T_c \sim 48 \text{ K})\) is unaffected by AF fluctuations.

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Since the discovery of superconductivity in the iron-based pnictide LaFeAsO\(_{1-x}\)F\(_x\) (F-doped La1111 series) \([1]\), extensive studies on various types of iron-based compounds have been conducted. To date, the Sm1111 series marks the highest superconducting (SC)-transition temperature \((T_c) (T_c=55 \text{ K})\) \([2]\). However, the 122 series has been mainly examined, as large single crystals are readily available \([3, 4]\). For the 122 series, an antiferromagnetic (AF) phase is followed by an SC phase with increasing carriers. The coexistence of these two phases near the phase boundary suggests an intimate interrelationship, indicating that AF fluctuations may be deeply associated with the SC mechanism.

However, exotic phase diagrams have been discovered for several compounds, such as the H-doped R1111 series \((R=\text{Ce, Sm, Gd})\) \([5, 6]\), the P-doped La1111 series \([7]\), FeSe [8-10], and R\(_{1-x}\)Fe\(_x\)-ySe\(_2\) \((R=\text{K and Tl}_{0.6}\text{Rb}_{0.4})\) \([11]\). The phase diagrams of these compounds are not explainable within a conventional framework, where a single SC phase follows a single AF phase by tuning parameters such as the doping level or pressure. Among these examples, the H-doped R1111 series is relatively simple because chemical tuning is performed only via the hydrogen doping of RO layers; consequently, the FeAs layers are free from local disturbance and randomness. Hydrogen can be doped in a wide doping range, leading to a new AF phase in a heavily doped regime [12-14]. That is, the SC phase is sandwiched between two AF phases in the phase diagram. Note that the H-doped R1111 series \((R=\text{Ce, Sm, Gd})\) has an SC dome with a \(T_c\) ranging from 45 to 50 K \([6]\). The SC dome moves to a lightly H-doped regime in the order of Ce, Sm, and Gd. Unlike these compounds, the La1111 series exhibits double domes with a minimum \(T_c\) of 15 K. Upon applying pressure, the double domes transform into a single dome \([5, 15]\) with a high \(T_c\) like the other R1111 series \((R=\text{Ce, Sm, Gd})\). This single dome moves to a lightly H-doped regime under increasing pressure, suggesting that the application of pressure is equivalent to the R replacement with heavier elements. For instance, the SC dome observed for the La1111 series at 3.0 GPa is almost identical to that for the Ce1111 series at ambient pressure (0.1 MPa). The application of pressure is more advantageous than the R replacement, as the influence of magnetic R elements is excluded.

We investigated an interrelationship between the SC phase and the second AF phase in a heavily H-doped regime via nuclear magnetic resonance (NMR) measurements for \(^{75}\text{As}\) by comparing the phase diagram at 3.0 GPa with that at 0.1 MPa. \(^{75}\text{As}\)-NMR measurements for the powder samples were acquired using a conventional coherent-pulsed NMR spectral meter. The relaxation rate \((1/T_1)\) was measured using a conventional saturation-recovery method. \(^{75}\text{As}\)-NMR spectra for the powder samples exhibit double edges in the field-swept spectra due to the quadrupole interaction, and \(1/T_1\) was measured at the lower-field edge, where the FeAs planes are parallel to the applied field. A pressure of 3.0 GPa was applied using a NiCrAl-hybrid clamp-type pressure cell. We used a mixture of Fluorinert FC-70 and FC-77 as the pressure-mediation liquid. A coil wound around the powder samples and an optical fiber with the Ruby powders glued on top were inserted into the sample space of the pressure cell. The pressure was monitored through Ruby fluorescence measurements [16].

The relaxation rate divided by temperature \((T)\), writ-
The sharp peaks in Figs. 1(a) and 1(b) indicate the Neel temperature, $T_N$. The arrows in Figs. 1(f), 1(g), 1(h), and 1(i) indicate the SC transition temperature. In a heavily H-doped regime, the second AF phase emerges accompanied with a round peak of $T_N$ (Figs. 1(j), 1(k), and 1(l)).

Figures 1(a)-1(l) show the evolution of $1/T_1T$ measured at both 0.1 MPa and 3.0 GPa for several F or H doping levels. For F doping, the maximum doping level is less than $x=0.14-0.15$ [18-20]. First, we focus on $1/T_1T$ at 0.1 MPa. For undoped and poorly F-doped regimes ($x < 0.05$), $1/T_1T$ exhibits an upturn toward the Neel temperature ($T_N$), and diverges or adopts a maximum at $T_N$.

$$\frac{1}{T_1T} \sim \frac{1}{T - T_N} + \text{const.} \quad (1)$$

For the case where AF fluctuations are weak or absent, $1/T_1T$ no longer exhibits the upturn, but instead, obeys the Korringa relation, which is proportional to the square of the density of states (DOS):

$$\frac{1}{T_1T} \sim \sum_i n_i(\varepsilon_F)^2, \quad (2)$$

where $n_i(\varepsilon_F)$ represents the DOS for the $d_{xy}$, $d_{yz}$, and $d_{zx}$ orbits of Fe ions.

$\text{FIG. 1: Evolution of } 1/T_1T \text{ for } T_{\text{He}}$ with respect to F or H doping levels (denoted by $x$) at ambient pressure (0.1 MPa) and 3.0 GPa. The sharp peaks in Figs. 1(a) and 1(b) indicate the Neel temperature, $T_N$. The arrows in Figs. 1(f), 1(g), 1(h), and 1(i) indicate the SC transition temperature. In a heavily H-doped regime, the second AF phase emerges accompanied with a round peak of $T_N$ (Figs. 1(j), 1(k), and 1(l)).
When pressure is applied, remarkable features appear in two regimes: \( x = 0.14-0.20 \) and \( x \geq 0.49 \). For \( x = 0.14-0.20 \), the minimum \( T_c \) at 0.1 MPa changes the maximum \( T_c \) and reaches 48 K, which is comparable to the highest \( T_c \) of 55 K (see Fig. 1(g)). For \( x \geq 0.49 \), the second AF phase is strongly suppressed when pressure is applied. These remarkable features are clearly seen from the color maps in Figs. 2(a)-2(d).

The absolute values of \( 1/T_1 T \) at 0.1 MPa and 3.0 GPa are plotted in Figs. 2(a) and 2(b), respectively, and the derivatives of \( 1/T_1 T \) with respect to temperature, i.e., \( \frac{d}{dT}(1/T_1 T) \), at 0.1 MPa and 3.0 GPa are plotted in Figs. 2(c) and 2(d), respectively. In a paramagnetic state above \( T_N \), \( \frac{d}{dT}(1/T_1 T) \) becomes negative (shown in red), whereas for both the SC and AF states, \( \frac{d}{dT}(1/T_1 T) \) becomes positive due to the decrease of quasi-particles or magnetic excitations at low temperatures. The SC domes appear to have no direct correlation with AF fluctuations or AF phases. Both the minimum \( T_c \) at 0.1 MPa and the maximum \( T_c \) at 3.0 GPa are observed within the same region, where the absolute values of \( 1/T_1 T \) are small and AF fluctuations are absent, shown in blue in Figs. 2(a) and 2(b). The areas in blue also correspond to the region where the resistivity of the powder samples exhibits a \( T^2 \) temperature dependence [25], suggesting a Fermi liquid state.

Detailed phase diagrams for the heavily H-doped regime \((x \geq 0.49)\) are shown in Figs. 3(b) and 3(c). The excitation gap \( \Delta \) of the AF state (Fig. 3(a)) is estimated using the following formula:

\[
\frac{1}{T_1 T} \sim e^{-\Delta/T} + \text{const.} \tag{3}
\]

The gap \( \Delta \) represents the order parameter of the AF phase, and becomes zero at \( x \sim 0.49 \) at 0.1 MPa. The data of \( T_c \) and \( T_N \) in Figs. 3(b) and 3(c) are determined based on the \( T \) dependence of \( 1/T_1 T \). In Fig. 3(d), the round peak corresponds to \( T_N \), whereas the onset of the sharp drop below 4 K corresponds to \( T_c \). The second AF phase is strongly suppressed at 3.0 GPa, and apparently shifts to a highly H-doped regime in the \( x-T \) phase diagram. For \( x = 0.49 \) and \( x = 0.51 \), a quantum phase transition form the AF to SC phases occurs; the AF phase with a \( T_N \) of 60-70 K vanishes, while instead the SC phase accompanied by a very low \( T_c \) emerges at 3.0 GPa. The phase transition from the AF to SC phases no longer occurs for \( x \geq 0.6 \) (see the round peaks in Fig. 3(c)).

The phase diagram at 3.0 GPa, as illustrated in Fig. 3(c), is highly important with respect to the quantum critical point (QCP) where the AF state disappears. The AF state disappears at the QCP due to a mismatching of the nesting conditions between electron pockets [26, 27] and/or broadening of the d-orbital bandwidth [28]. A "bare" QCP emerges under pressure owing to the phase segregation between the AF and SC phases. A fan-shaped nobel quantum critical regime is theoret-
FIG. 3: Excitation gap, phase diagrams, and $1/T_1 T$ for a heavily H-doped regime. (a) The excitation gap $\Delta$ is estimated from Eq. (3). (b) Electronic phase diagram for a heavily H-doped regime determined from the $1/T_1 T$ of $^{75}$As at 0.1 MPa. (c) The phase diagram determined from the $1/T_1 T$ of $^{75}$As at 3.0 GPa. The portion colored in green shows the SC phase induced under pressure. The paramagnetic state in yellow shows the quantum critical regime. (d) $1/T_1 T$ of $^{75}$As for 51% H-doped samples. The inset is an expansion of $1/T_1 T$ measured at 3.0 GPa. The arrows indicate the superconducting transition temperature ($T_c$) and the Neel temperature ($T_N$). (e) $1/T_1 T$ of $^{75}$As for 60% H-doped samples.

In summary, we have studied the second AF phase of H-doped LaFeAsO under pressure via $^{75}$As-NMR techniques. The second AF phase is strongly suppressed under pressure, thereby a "bare" QCP emerges. A pressure-induced quantum phase transition from the AF to SC phases occurs in a narrow doping regime near the QCP. The quantum critical regime emerges in a wide $T$ region above the QCP. However, the influence of the AF critical fluctuations to the SC phase is limited in the narrow doping regime near the QCP. The optimal $T_c$ condition is unaffected by AF fluctuations, implying the existence of competing pairing interactions in the SC phase.

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