On the origin of critical nematic fluctuations in pnictide superconductors

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We employ polarization-resolved Raman spectroscopy to study critical nematic fluctuations in Ba(Fe1−xAu)x2As2 superconductors above and across well separated tetragonal to orthorhombic phase transition at temperature TS(x) and the Néel transition at TN(x). The static Raman susceptibility in XY symmetry channel increases upon cooling from room temperature following the Curie-Weiss law, with Weiss temperature TS(x) several tens of degrees lower than TN(x). Data reveals a hidden nematic quantum critical point at xe = 0.031 when the system becomes superconducting, indicating a direct connection between quantum critical nematic fluctuations and unconventional superconductivity. We attribute the origin of the nematicity to charge quadrupole fluctuations due to electron transfer between the nearly degenerate dxz/dyz orbitals.

It is widely believed that the interactions leading to high-temperature superconductivity are already present in the parent compounds. The parent compounds of the Fe-based superconductors usually show a tetragonal to orthorhombic structural transition at temperature TS that is accompanied by transition into collinear antiferromagnetic phase at temperature TN, typically only slightly lower than TS.

Recently, much attention was devoted to studies of non-symmetric dynamical fluctuations above TS which break local four-fold symmetry, usually referred as nematic fluctuations [1]. Below TS, significant anisotropy was found for properties measured along the two planar orthogonal Fe-Fe directions, notably in electrical resistivity [2], optical conductivity [3], thermopower [4], and local density-of-states (DOS) [5]. It has been established both by the static probes such as shear modulus C66 [6–9], Young’s modulus Y110 [10, 11], the elasto-resistance coefficient m66 [12, 13], and by the dynamic probe: polarization resolved Raman scattering [14–22], that the underlying nematic fluctuations have a distinct XY quadrupole symmetry and that they extend to temperatures far above TS. However, the origin of the nematic fluctuations remains under debate.

Among interpretations, it has been proposed that the fluctuations could originate from charge transfer between degenerate dxz/dyz orbitals [16, 23–30], or from magnetic interactions [31–38]. We noticed that for Ba(Fe1−xAu)x2As2 superconductors the TS and TN transition temperatures are well separated, thus the system provides a platform to study separately the charge and spin contributions to the nematic fluctuations.

In this Letter, we use the static Raman susceptibility derived from the dynamical response acquired in the XY-symmetry quadrupole channel to study the evolution of the nematic fluctuations above and across the
FIG. 2. Temperature dependence of the Raman response $\chi''_{\omega}(\omega, T, x)$ for Ba(Fe$_{1-x}$Au$_x$)$_2$As$_2$. (a)-(c) $x = 0$, (d)-(f) $x = 0.012$, (g)-(i) $x = 0.014$ and (j)-(l) $x = 0.031$. The arrow in (a) indicates the QEP.

Table I. Summary of the structural and magnetic phase transitions as function of Au doping into Ba(Fe$_{1-x}$Au$_x$)$_2$As$_2$ crystals. Above $T_S$, the static Raman susceptibility follows the Curie-Weiss law with Weiss temperature $T_\theta(x)$ about 40-60 K lower than $T_S$. The growth of susceptibility stops below $T_S$, when degeneracy of the $d_{xz}$ and $d_{yz}$ orbitals is lifted, emphasizing a relation between nematicity and $d$-wave (SDW) gap is depleting the DOS of the occupied magnetic order parameter develops and as a spin-density-wave (SDW) gap is depleting the DOS of the occupied $d_{xz}/d_{yz}$ orbitals.

Single crystals of Ba(Fe$_{1-x}$Au$_x$)$_2$As$_2$ ($x = 0, 0.012, 0.014, 0.031$) were grown out of self-flux using a high-temperature solution growth technique described in Refs. [41, 42], and the chemical compositions were determined by energy dispersive spectroscopy (EDS) analysis. The room-temperature crystal structure, illustrated in the inset of Figs. 1(a), belongs to space group $I4/mmm$ (point group $D_{4h}$). The $T_S$ and $T_N$ of the Au-doped samples were determined, respectively, by the temperature evolution of the neutron nuclear and the magnetic Bragg peak intensities shown in Figs. 3(f)-3(h). For the pristine compound, $T_S \approx T_N = 135$ K, as was determined by bulk property measurements [42], in agreement with neutron diffraction measurements [43]. The $T_S$ and $T_N$ values for the compositions studied are summarized in Table I.

The crystals used for Raman scattering were cleaved and positioned in a continuous helium flow optical cryostat. The measurements were performed in a quasi-back scattering geometry along the crystallographic $c$-axis using the Kr$^+$ laser line at 647.1 nm (1.92 eV). The excitation laser beam was focused into a $50 \times 100$ $\mu$m$^2$ spot on the $ab$-surface, with the incident power around 10mW. The scattered light was collected and analyzed by a triple-stage Raman spectrometer designed for high-stray light rejection and throughput, and then recorded using a liquid nitrogen-cooled charge-coupled detector. Raman scattering intensity data were corrected for the spectral responses of the spectrometer and detector. The laser heating in the Raman experiments is determined by imaging the appearance of stripes due to twin domain formation at the structural phase transition temperature $T_S$ [17]. When stripes appear under laser illumination, the spot temperature is just slightly below $T_S$, thus $T_S = kP + T_{cryo}$, where $T_{cryo}$ is the temperature...
of cold helium gas in the cryostat, $P$ is the laser power and $k$ is the heating coefficient. By recording $T_{exp}$ when the stripes appear at different laser powers, we can deduce the heating coefficient using a linear fit: $k = 1 \pm 0.1$ K/mW.

We define $X$ and $Y$ directions along the 2-Fe unit cell basis vectors (at 45° from the Fe-Fe direction) in the tetragonal phase, whereas $X'$ and $Y'$ are along the Fe-Fe directions, as shown in the inset of Fig. 1(a). According to Raman selection rules, the $XX$, $XY$, $X'Y'$, $X'Y'$ scattering geometries probe $A_{1g} + B_{1g}$, $A_{2g} + B_{2g}$, $A_{1g} + B_{2g}$ and $A_{2g} + B_{1g}$ symmetry excitations of the $D_{4h}$ point group respectively. The data in the $XY'(B_{1g})$ symmetry channel barely changes with temperature [Fig. 1(a)]. In contrast, the spectrum in the $XY(B_{2g})$ symmetry channel show strong temperature dependence [Fig. 1(b)]. Therefore, we subtract the background signal recorded in the $XY'$ geometry from the data measured in the $XY$ geometry to obtain $\chi''_{B_{2g}}(\omega, T)$ response function [14].

In Figs. 2(a)-2(c), we show the Raman response for BaFe$_2$As$_2$ in the $B_{2g}$ channel at temperatures between 300 K and 15 K. The most remarkable feature appearing upon cooling is a quasi-elastic peak (QEP) that reaches its maximum intensity around $T_S/T_N$ [Fig. 2(a)]. The QEP is sharply suppressed within 5 K below $T_S/T_N$ [Fig. 2(b)] and it vanishes at lower temperatures [Fig. 2(c)]. Above $T_S(x)$, the Raman response for the Au-doped samples ($x = 0.012, 0.014, 0.031$) shows similar behavior as for the pristine compound [Figs. 2(d), 2(g) and 2(j)]. Unlike for the pristine compound, $T_S(x)$ $\neq T_N(x)$ in the doped samples. Interestingly, the passage across $T_S(x)$ does not affect the Raman response significantly, as shown in Figs. 2(e), 2(h) and 2(k). The situation is quite different when temperature decreases below $T_N(x)$ [Figs. 2(f), 2(i) and 2(l)]. As with the pristine compound, the QEP is suppressed quickly upon cooling below $T_N(x)$.

For better understanding of QEP evolution in the $B_{2g}$ channel, we compute the static nematic susceptibility $\chi'_{B_{2g}}(0, T, x)$ from the experimental data using the Kramers-Kronig transformation [14, 19, 20]:

$$\chi_{B_{2g}}(0, T, x) \approx \frac{2}{\pi} \int_0^{350 \text{ cm}^{-1}} \frac{\chi''_{B_{2g}}(\omega, T, x)}{\omega} d\omega.$$  

The integral underlines importance of Raman response in low-frequency limit. We use linear extrapolation for response below 8 cm$^{-1}$ instrumental cut-off.

In Figs. 3(a)-3(l), we show temperature dependence of $\chi_{B_{2g}}(0, T, x)$. Above $T_S(x)$, the static Raman susceptibility is well described by the Curie-Weiss law

$$\chi_{B_{2g}}(0, T, x) \propto Q^2(x)/(T - T_w(x)),$$

where $T_w(x)$ is the Weiss temperature and square of the charge quadrupole moment $Q^2(x)$ is proportional to Curie constant [22]. This fit is better expressed by the linear behavior of the inverse susceptibility, $\chi_{B_{2g}}^{-1}(0, T, x)$.
The values of $T_\theta(x)$, which correspond to the abscissae of the linear fits, are given in Table I and shown in Fig. 4 [44].

$T_\theta(x)$ is monotonically decreasing function of $x$, at about 40-60 K lower than $T_S(x)$. At a critical doping $x_c = 0.031$ the Weiss temperature approaches zero, indicating a hidden quantum critical point. At this critical Au-doping concentration the system is a superconductor with $T_c = 2.5$ K [42], indicating a strong connection between quantum critical nematic fluctuations and unconventional superconductivity [2, 45].

For pristine BaFe$_2$As$_2$, susceptibility $\chi_{B_{2g}}(0, T, x = 0)$ is rapidly suppressed just below $T_S/T_N$. In contrast, for the Au-doped samples, $\chi_{B_{2g}}(0, T, x > 0)$ has a plateau-like saturation between split $T_S(x)$ and $T_N(x)$, with only a slight decrease, followed by much faster decrease below $T_N(x)$ to a saturation value at temperature coinciding with magnetic order parameter saturation temperature, Figs. 3(e)-3(h).

The fact that the static susceptibility stops increasing on cooling below $T_S$, when $T_N$ is lower than $T_S$, indicates that the origin of the critical fluctuations is not magnetic but rather is driven by the charge quadrupole fluctuations [19, 20, 22]. The likely scenario for quadrupole charge fluctuations with $B_{2g}$ symmetry is a charge transfer between the nearly degenerate $d_{xz}$ and $d_{yz}$ orbitals. Such quadrupole charge fluctuations are expected to slow down below $T_S$, when the degeneracy of $d_{xz}/d_{yz}$ orbitals is lifted, and be suppressed below $T_N$, when the SDW gap depletes the electronic DOS at the Fermi level, with complete suppression when the magnetic ordering is fully established.

In more details, the electron transfer between quasi-degenerate $d_{xz}/d_{yz}$ orbitals induces a charge quadrupole moment $Q(x)$ proportional to the local charge imbalance $n_{xz} - n_{yz}$. The charge quadrupole moment can be estimated from the fitted Curie constant, Eq. (2). The $Q(x)$ values for Ba(Fe$_{1-x}$Au$_x$)$_2$As$_2$ are summarized in Table I. In the inset of Fig. 4, we show the doping dependence of $Q(x)$ and of the ordered magnetic moment $M(x)$ as a function of Au concentration $x$. The opposite doping dependence of the charge quadrupole moment $Q(x)$ and of the magnetic moment $M(x)$ suggests that the charge quadrupole order at the Fe site competes with stripe magnetic order. Some conclusion can be reached from the fact that the static XY quadrupole susceptibility saturates at $T_S$ and is gradually suppressed below $T_N$ as the stripe magnetic order parameter builds up.

In conclusion, we studied nematic Raman response for Au-doped BaFe$_2$As$_2$ samples, which have split structural and magnetic transition temperatures. The data revealed that above $T_S$ the static Raman susceptibility in the quadrupole $B_{2g}$ channel follows a Curie-Weiss behavior. Between $T_S$ and $T_N$, the susceptibility stops increasing, and it decreases only below $T_N$, when the magnetic order parameter develops and a SDW gap opens. We attribute the corresponding increase of the Raman susceptibility to quadrupole charge fluctuations due to electron transfer between nearly degenerate $d_{xz}$ and $d_{yz}$ orbitals. Weiss temperature $T_\theta(x)$ extrapolated from the high-temperature fluctuations is decreasing with doping concentration $x$ and is several tens of degrees lower than $T_S(x)$ and $T_N(x)$. Importantly, the critical concentration $x_c$ defining the quantum critical point $T_\theta(x_c) = 0$ is located inside the small superconducting dome, thus underlining the role played by the quadrupole orbital fluctuations in the pairing mechanism of the Fe-based superconductors [2, 45]. The extrapolated charge quadrupole moment $Q(x)$ is monotonically increasing function, while the ordered magnetic moment $M(x)$ is a decreasing function of $x$, suggesting that the charge quadrupole order competes with the collinear antiferromagnetic order.

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