Collapse of nematic fluctuations in FeSe under pressure

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We report the evolution of the electronic nematic susceptibility in FeSe via Raman scattering as a function of hydrostatic pressure up to 5.8 GPa where the superconducting transition temperature $T_c$ reaches its maximum. The critical nematic fluctuations observed at low pressure quickly vanish above 1.6 GPa, indicating they play a marginal role in the four-fold enhancement of $T_c$ at higher pressures. The collapse of nematic fluctuations appears to be linked to a suppression of low energy electronic excitations which manifests itself by optical phonon anomalies at around 2 GPa, in agreement with lattice dynamical and electronic structure calculations using local density approximation combined with dynamical mean field theory. Our results reveal two different regimes of nematic fluctuations in the phase diagram of FeSe under pressure, and shed new light on the interplay between nematicity, magnetism and superconductivity in iron based superconductors.

The pairing mechanism of iron-based superconductors (Fe SC) is believed to result from interband spin fluctuations [1,2]. The spin fluctuations scenario is motivated by the observation that the maximum superconducting transition temperature corresponds to the end point of a stripe-like magnetic phase in several Fe SC [3]. However the magnetic order is invariably preceded by, or concomitant with, an electron nematic phase whereby the electronic sub-system spontaneously breaks the fourfold tetragonal symmetry and induces an orthorhombic distortion of the lattice [4,5]. In several Fe SC strong electron nematic fluctuations (NF) have been observed near the optimal critical temperature $T_c$ [6,8], hinting that they could play a role too in the pairing mechanism. Recent theoretical works indeed support the idea that NF are generically helpful for SC pairing, providing a complementary, or possibly alternative, route to high-$T_c$ SC [9,10]. However disentangling the respective roles of the intertwined magnetic and nematic fluctuations in enhancing $T_c$ remains a challenge in many Fe SC.

In this context superconducting FeSe stands out for its unusual properties compared to other Fe SC [11]. In bulk form and at ambient pressure, it displays a nematic phase without any sign of magnetic ordering, but with a relatively low $T_c$ (9 K) [12,13]. However $T_c$ is strongly enhanced in monolayer form reaching at least 70 K [17], and also under strong electron doping with $T_{c,\text{max}} \sim 40$ K [18,21]. In both cases the absence of hole pockets at the $\Gamma$ point seems at odds with the interband magnetic pairing scenario [22,24], which however could be operative even in that case [25].

A similar increase of $T_c$ is also observed upon applying hydrostatic pressure, reaching $\sim 37$ K at $\sim 6$ GPa [26,27] (figure [1]). Here also the underlying pressure phase diagram of FeSe differs significantly from other prototypical Fe SC [28,32]. The nematic phase transition temperature $T_S$ initially decreases with pressure, and merges with a pressure induced magnetic phase at around 1.5 – 2 GPa. The magnetic phase displays an orthorhombic distortion and is likely similar to the stripe-ordered phase observed in other Fe SC [31,33]. The coupled magneto-structural transition temperature ($T_{S,m}$) has a non-monotonic pressure dependence terminating close to optimal pressure where $T_c$ is maximum [30], questioning the respective roles of magnetic and nematic fluctuations in the pressure-induced four-fold enhancement of $T_c$.

Recently ARPES and transport measurements have suggested a possible link between the increases of $T_c$ and changes in Fermi surface topology [20,34,35]. However little is known about the corresponding evolution of relevant fluctuations. Magnetic fluctuations have been probed in the low pressure / low $T_c$ range by NMR [33,36], but the pressure evolution of NF has not been addressed.

In this letter we report the temperature and pressure dependence of the NF in bulk FeSe single crystals using Raman spectroscopy up to 5.8 GPa. We show that the NF disappear rapidly upon increasing pressure and essentially vanish above 1.6 GPa, in the pressure range where the nematic and magnetic transitions merge, indicating two different regimes of nematicity and implying a marginal role of NF in the enhancement of $T_c$ at higher pressures. We further show that the disappearance of the NF is accompanied by anomalies in the pressure dependence of Raman-active optical phonon frequencies. Supported by density functional theory plus dynamical mean-field theory calculations, we link the phonon anomalies and the collapse of NF at low pressure to a Lifshitz transition in the electronic structure, where a hole pocket moves below the Fermi energy upon increasing pressure.
Raman measurements under pressure were performed using a membrane diamond anvil cell (DAC) allowing continuous change of pressure at low temperature, and designed with a large numerical aperture as described in [37, 38]. Helium was used as the pressure transmitting medium. Figure 1(b) shows a sketch of the pressure cell and a photograph of the sample inside the cell. Focus was made on Raman spectra taken in the $B_{1g}$ symmetry [39] which, in the 1-Fe unit cell notation, corresponds to the nematic order observed in FeSe at ambient pressure [40].

Figure 1(c) displays the temperature dependence of the Raman response in $B_{1g}$ symmetry at 0.3 GPa. It follows the behavior of the Raman spectra of FeSe at ambient pressure reported earlier [40]. When approaching the nematic transition from high temperatures, the growth of NF manifests itself by an increase in the low energy Raman response $\chi''(\omega)$ upon approaching $T_S$, and a subsequent decrease in the nematic phase below $T_S$. The evolution of the low energy response was followed as a function of temperature and pressure in $B_{1g}$ symmetry. In order to account for small variations in the global intensity of the signal between different pressures due to changes in the optical alignment, the Raman spectra at each pressure were divided by a reference value, taken to be the value of the Raman response at 103 K and 450 cm$^{-1}$ [39].

The temperature dependence of the $B_{1g}$ Raman conductivity $\chi''/\omega$, which controls the static nematic susceptibility (see equation (4) below), at six different pressures between 0 GPa and 3.0 GPa is plotted in figure 1(d). For clarity only spectra above the estimated $T_S$, which is 89 K at 0 GPa but decreases when increasing pressure [29, 41], are shown. The spectra at 0 GPa were taken outside the pressure cell on a different crystal from the same batch, and are shown here for comparison. In the Raman conductivity spectrum the NF appear as a quasi-elastic peak (QEP) centered at zero-energy [42].
Figure 2. (a) Temperature dependence of the static nematic susceptibility $\chi_0^{B_{1g}}$ at different pressures between 0 and 5.8 GPa. Dashed lines are linear fits showing the slope at 100 K: $\frac{d\chi_0^{B_{1g}}}{dT}$ at each pressure from 0 to 1.6 GPa; within experimental accuracy, the slope is 0 above 3 GPa. (b) Color map of the static nematic susceptibility $\chi_0^{B_{1g}}$ as a function of temperature and pressure, plotted using the data points in (a). The color scale is in arbitrary units. The structural ($T_S$), magnetic ($T_m$) and magneto-structural ($T_{S,m}$) transition temperatures are indicated by black, purple and orange symbols respectively. Full squares: this work; empty diamonds: [31]; empty triangles: [33]. Red squares with error bars indicate the pressure range of the phonon anomalies at 103 K, 53 K and 20 K (see text).

At low pressures, below 0.8 GPa, the QEP intensity increases significantly when lowering temperature down to $T_S$, following the behavior observed at ambient pressure. However upon increasing pressure the maximum intensity of the QEP close to $T_S$ (blue curve at each pressure), and its overall enhancement decrease significantly. At 1.6 GPa and 3.0 GPa the QEP is barely visible and shows negligible enhancement upon cooling.

In order to quantify the observed pressure evolution of NF, we computed the static $B_{1g}$ nematic susceptibility $\chi_0^{B_{1g}}$, obtained from the Raman conductivity through the Kramers-Kronig relation:

$$\chi_0(T,P) = \int_0^\infty \frac{\chi''(\omega,T,P)}{\omega} \, d\omega$$  \hspace{1cm} (1)

The integral was performed over the whole frequency range accessible from our data, i.e. from 0 to 470 cm$^{-1}$, with the data at low energy resulting from linear extrapolation of the Raman response between 0 and 12 cm$^{-1}$ (19 cm$^{-1}$ below 0.8 GPa). The resulting temperature dependence of the nematic susceptibility at each pressure is plotted in figure 2(a) where we have included additional points at higher pressures: 4.2 GPa and 5.8 GPa. At low pressures $\chi_0^{B_{1g}}$ increases when lowering temperature, reaches a maximum at $T_S(P)$ and decreases inside the nematic phase. The general trend of $\chi_0^{B_{1g}}$ as a function of pressure clearly indicates a decrease of the nematic susceptibility upon increasing pressure. The loss of nematic susceptibility is mirrored in its temperature dependence: while its increase when lowering temperature is still significant at 0.8 GPa, indicating sizable critical NF close to $T_S$ at this pressure, it is much weaker at 1.6 GPa and there is essentially no increase at 3 GPa and above. Besides, at 4.2 GPa and 5.8 GPa the static susceptibility shows a small but clear suppression below ~40 K and ~60 K respectively, which might be linked to the magneto-orthorhombic transition.

The evolution of $\chi_0^{B_{1g}}$ with temperature and pressure is summarized in a colormap phase diagram in figure 2(b). Also plotted are the values of the structural ($T_S$), magnetic ($T_m$) and magneto-structural ($T_{S,m}$) transitions as reported in [31, 33], along with the structural transition temperatures extracted from our data as the temperature at which $\chi_0^{B_{1g}}$ is maximum. The latter are consistent with those of [31, 33], except at 1.6 GPa where our value appears somewhat higher.

The absence of NF above ~1.6 GPa implies that they play a marginal role in the enhancement of $T_c$ observed between 2 and 6 GPa [30, 41]. In particular the behavior at 5.8 GPa, where $T_c$ reaches its maximum, is in striking contrast with the divergent nematic susceptibility observed near $T_{c,max}$ in several Fe SC [6, 8, 43]. It is noteworthy that the disappearance of NF coincides with the merging of the magnetic and structural transitions into a coupled first-order transition, which occurs between 1.5 GPa and 2.0 GPa (see figure 2(b)) [31, 33]. As we show below, the evolution of optical phonons under pressure points to a change in the low energy band structure in the same pressure range, providing an underlying cause for these phenomena.

In figure 3 we plot the pressure evolutions of the frequencies of two Raman active phonons at two different temperatures: 103 K and 20 K. The $A_{1g} / B_{2g}$ symmetry phonon involves the motion of the Selenium / Iron atoms out of plane. Between 2 GPa and 8 GPa...
the phonon frequencies display a linear pressure hardening consistent with lattice contraction. However below 2 ± 0.5 GPa a clear frequency softening, which manifests itself by a deviation from linearity in the pressure dependence, is observed for both phonons. For the $B_{2g}$ Fe phonon a linewidth broadening is also observed \[59\]. Importantly, while the observed deviations are stronger at 20 K, they are also visible at 53 K \[39\] and 103 K, implying that they are not mere consequences of the magneto-structural transition nor of the superconducting transition, which respectively occur below 60 K and 40 K at all pressures \[28\] \[30\] \[31\] \[41\]. We note that anomalies of the structural parameters have been reported in the same pressure range at low temperature \[32\] \[34\].

In order to clarify the origin of the phonon anomalies, we performed theoretical calculations of the band structure and the phonon energies under pressure, using local density approximation combined with dynamical mean-field Theory (LDA+DMFT, figure 4a, b) \[46\] in the paramagnetic state (PM). Remarkably the calculations display a clear softening of both phonon frequencies at \(~ 2\) GPa. In this pressure range, the calculated electronic structure undergoes a Lifshitz transition due to the disappearance of the inner hole pocket at the $\Gamma$ point between 1.9 GPa and 2.6 GPa (fig. 4c), see also \[47\], suggesting the phonon anomalies are associated to a change in Fermi surface topology \[48\]. On the other hand, the phonon frequencies calculated using DFT in the general gradient approximation (GGA) in the stripe magnetic phase, where no Lifshitz transition occurs, do not show any significant anomaly in the whole pressure range investigated (figure 4). The occurrence of phonon anomalies at a pressure induced Lifshitz transition is not new, and has been argued to occur in several systems, notably MgB$_2$ and “Bi2212” cuprate superconductors \[49\] \[50\]. In this scenario the phonon softening below \(~ 2\) GPa is associated to the emergence of additional low energy electronic excitations to which the optical phonons couple \[51\] \[52\].

We note that in contrast to our LDA+DMFT calculations, the inner-hole band has been reported by ARPES to be already slightly below the Fermi level at ambient pressure \[53\] \[55\]. However the shift of the inner-hole band will not only suppress the inner-hole intraband excitations, but also the low energy interband excitations between the inner and outer hole bands as their splitting near the $\Gamma$ point increases with pressure (see figure 4c and also \[56\]). The latter contribution to the electron-phonon coupling is operative even if the inner-
hole band is incipient, but is suppressed when the band moves deeper below the Fermi level. Moreover, strong anharmonic effects are generically expected close to a Lifshitz transition, where phonon atomic displacements can move entire bands across the Fermi level [39, 57]. They could also play a role in the experimental low-pressure phonon softening reported here.

While the behavior of phonons alone cannot fully ascertain the exact nature of the change in the low energy band structure between 0 and 2 GPa, our data suggest an intriguing link between this change and the strength of NF. The link appears clearly when plotting together the evolution under pressure of the Fe phonon frequency and that of the slope of the nematic susceptibility, both at 103 K (figure 3b): the latter goes to zero in the same pressure interval where the former recovers linearity. This suggests that the low energy electronic states responsible for the phonon softening at low pressure also drive strong NF, causing the coupled first-order magneto-structural transition to split into two separate transitions below \( \sim 2 \) GPa. Several theoretical studies have shown that the strength of the nematic and magnetic couplings strongly depend on the size and the nesting conditions of the hole and electron pockets [53, 64]. Interestingly these studies have generally neglected the impact of incipient bands, whose role in driving high-\( T_c \) phase in FeSe monolayer has been recently shown to be crucial [25].

Our work calls for further theoretical developments on the key ingredients of the band structure near the Fermi level in setting the dominant interactions that govern the phase diagram of bulk FeSe and promote its high \( T_c \) superconducting phase.

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The authors declare no competing interests.

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