Nematic susceptibility of hole- and electron-doped BaFe$_2$As$_2$ iron-based superconductors

A. E. Böhmer, P. Burger, F. Hardy, T. Wolf, P. Schweiss, R. Fromknecht, M. Reinecker, W. Schranz, and C. Meingast

1 Institut für Festkörperphysik, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
2 Fachbereich für Physik, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany
3 Faculty of Physics, University of Vienna, Boltzmanngasse 5, Vienna A-1090, Austria

(Dated: May 16, 2013)

The nematic susceptibility, $\chi_\phi$, of hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ iron-based superconductors is obtained from measurements of the elastic shear modulus using a three-point bending setup in a capacitance dilatometer. Nematic fluctuations, although weakened by doping, extend over the whole superconducting dome in both systems, suggesting their close tie to superconductivity. Evidence for quantum critical behavior of $\chi_\phi$ is surprisingly, only found for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, the system with the lower maximal $T_c$ value.

PACS numbers: 74.25.Ld, 74.40.Kb, 74.62.Fj, 74.70.Xa

As in many other unconventional superconductors, superconductivity in iron-based superconductors arises close to the point where an antiferromagnetic (AFM) spin-density-wave transition (SDW) is suppressed [1, 2]. A particular feature of the iron-based materials is that the SDW breaks the four-fold rotational symmetry of the lattice which is accompanied by an orthorhombic distortion [2]. The fact that the structural transition surprisingly precedes the SDW transition in some systems has led to a strong debate about the driving force of the structural phase transition; e.g., orbital [3–5] or spin-nematic [6] degrees of freedom have been proposed. Importantly, orbital or spin fluctuations are also likely candidates for the superconducting pairing glue [8, 9]. Whereas magnetic fluctuations are believed to mediate $s_\pm$-superconductivity [8, 10, 11], orbital fluctuations are thought to lead to $s_{+\pm}$-superconductivity [12, 13]. The structural transition in the Fe-based materials is of strong current interest [7, 12, 15], because it is believed to be of an electronic nematic type, i.e., a transition in which the electronic degrees of freedom cause a spontaneous breaking of the four-fold lattice symmetry. Such nematic transitions are believed to also occur also in Sr$_3$Ru$_2$O$_7$ and the cuprate superconductors [16, 17].

Recently, the nematic susceptibility of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (Co-Ba122) has been obtained indirectly from measurements of the uniaxial-strain derivative of the resistivity anisotropy, and the intensity of nematic fluctuations was found to reach a maximum near optimal doping [15]. Measurements of the elastic shear modulus $C_{66}$, which is the soft mode associated with the structural transition, on the other hand, also provide a powerful tool for studying nematic fluctuations in detail [18, 19]. In particular, the softening of $C_{66}$ was studied intensively in Co-Ba122 using ultrasound, and strong evidence for a quantum critical point (QCP) was obtained near optimal doping [20]. Further, the response of $C_{66}$ below the superconducting transition provides important information about the coupling of these fluctuations to superconductivity, which has been interpreted both in the spin-nematic and the orbital scenario [18, 20]. Up to the present, shear-modulus data have only been reported for the electron-doped Co-Ba122 system from ultrasound measurements. It is clearly of interest to establish whether the nematic susceptibility of other Fe-based superconductors shows similar behavior.

In this Letter we present an extensive study of the shear modulus of both hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (K-Ba122) and electron-doped Co-Ba122 covering a wide doping range. We use a newly developed technique, in which the elastic shear modulus $C_{66}$ is accessed via the system’s Young’s modulus measured with a three-point bending setup in a capacitance dilatometer. Three-point bending is less demanding in terms of samples than ultrasound and therefore allows us to study a larger variety of systems. We first demonstrate its effectiveness by showing that the ultrasound $C_{66}$ data in Co-Ba122 can be essentially reproduced, and then present new data for hole doped K-Ba122. We find that nematic fluctuations are enhanced over the whole superconducting dome of both systems, suggesting their close tie to superconductivity. Surprisingly, evidence for quantum critical behavior of the nematic susceptibility is only found for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, the system with the lower maximal $T_c$ value.

Self-flux grown single crystals of K-Ba122 and Co-Ba122 were cleaved and cut to a size of $L \times b \times h \sim (2 - 3 \times 1 \times 0.1)$ mm$^3$ with $h$ along the crystalline $c$ axis and $L$ along tetragonal [110]. The crystals were supported by three wires and then placed in the capacitance dilatometer [21] (see Fig. 1[a,b]), in which they naturally experience a small and roughly constant force of about 0.2 N due to the springs holding the upper capacitor plate. This force is normally used to hold the sample in place; here it acts to bend the sample slightly,
Young’s modulus along [110] direction [23]:

\[ Y_{[110]} \approx \frac{B}{E} + \frac{C_{66}^0}{E} \epsilon_6^2 - \lambda \varphi \epsilon_6, \]

\( Y \) to (see Fig. 1(b)), the bending spring constant method.

resolution data due to the sensitivity of the capacitance small and thin samples, this technique yields very high reported separately [22]. Besides being able to measure small and thin samples, this technique yields very high resolution data due to the sensitivity of the capacitance method.

For thin samples (h/L ≪ 1) in the proper orientation (see Fig. 1(b)), the bending spring constant \( k_b \) is related to \( Y_{[110]} \), the Young’s modulus (i. e. the modulus of elasticity for uniaxial tension) along the [110] direction [23]:

\[ k_b \approx 4b(h/L)^3Y_{[110]} \]

\( Y_i \) is the inverse of \( S_{ii} \), the relevant component of the elastic compliance tensor [23] so that for a tetragonal sample

\[ Y_{[110]} = 4 \left( \frac{1}{C_{66}} + \frac{1}{\gamma} \right)^{-1} \]

and \( Y_{[110]} \) is dominated by \( C_{66} \) as long as \( C_{66} \) is smaller than \( \gamma \). This certainly holds close to the structural transition, but, as we demonstrate on the Co-Ba122 system, our method yields very similar results as the ultrasound data over the whole doping range [20], suggesting that the temperature dependence of \( C_{66} \) may be obtained even far away from the structural transition. Fig. 1(c,d) shows the Young’s modulus \( Y_{[110]} \) of Co-Ba122 and K-Ba122, which was normalized at room temperature because of uncertainties in the geometrical parameters \( L, b \) and \( h \). Importantly, our data on Co-Ba122 agree very well with the \( C_{66} \) results of Ref. [20] over the whole doping range; for a direct comparison we have also plotted \( C_{66} \) data for \( x = 0 \) in Fig. 1(c).

Both characteristics of the electron-doped system, namely the softening on approaching the structural transition at \( T_s \) from above and the hardening below \( T_c \), are observed also in hole-doped K-Ba122. However, the softening and subsequent hardening, at e.g. optimal doping, is much more pronounced for Co- than for K-doping, which will be discussed in more detail later.

In general, the elastic constants associated with the soft mode are expected to go to zero at a second-order structural phase transition and to harden below. Surprisingly, this is not the case here and \( Y_{[110]} \), even though it decreases by 50-85%, never reaches zero, a behavior which is not fully understood and also observed in ultrasound data [20]. Also, we find that \( T_s \) manifests itself as a kink in \( Y_{[110]}(T) \) and, below \( T_s \), \( Y_{[110]} \) stays soft, or even grows softer, in agreement with Ref. [20] but contrary to the general expectation. In our case, this effect presumably arises from “superelastic” behavior [21, 22], i.e. from the motion of boundaries between structural twins that are formed in the orthorhombic phase.

As argued previously [15, 20], the structural transition in Ba122 is most likely driven by an electronic order parameter \( \varphi \) via bilinear coupling to the orthorhombic strain \( \epsilon_6 = (a - b)/(a + b) \). In this case the Landau expansion of the free energy is given by

\[ F = \frac{1}{2} \left( \frac{a}{b} \right)^{-1} \varphi^2 + \frac{B}{4} \varphi^4 + \frac{C_{66}^0}{6} \epsilon_6^2 - \lambda \varphi \epsilon_6, \]

where \( \lambda \) is the electron-lattice coupling constant and \( C_{66,0} \) the bare elastic constant, which has no strong tem-
temperature dependence. Bilinear coupling is allowed because $\varphi$ and $\varepsilon_0$ both break the same four-fold rotational symmetry. We therefore refer to $\varphi$ as the nematic order parameter with $\chi_\varphi$ the associated nematic susceptibility. $\varphi$ may represent e.g. the spin-nematic or the orbital order parameter, however, this thermodynamic treatment cannot distinguish between these scenarios. $C_{66}$ is renormalized due to the coupling $\lambda$\cite{18, 27, 28}, and is given by

$$C_{66} = C_{66,0} - \lambda^2 \chi_\varphi.$$  

At a mean field level, the temperature dependence of $\chi_\varphi$ is given by $\chi_\varphi = [A(T - T_0)]^{-1}$, reflecting that $\chi_\varphi$ diverges at the “bare” transition temperature $T_0$, i.e. the nematic ordering temperature in the absence of electron-lattice coupling. Due to the coupling $\lambda$, however, the ordering of $\varphi$ and the associated structural distortion takes place at $T_{s,CW}^* = T_0 + \lambda^2/AC_{66,0}$, the temperature at which $\chi_\varphi$ reaches the critical value $C_{66,0}/\lambda^2$. $C_{66}$ in turn follows the modified Curie-Weiss law

$$\frac{C_{66}}{C_{66,0}} = \frac{T - T_{s,CW}^*}{T - T_0}.$$  

The difference $T_{s,CW}^* - T_0 = \lambda^2/AC_{66,0}$ (the “Jahn-Teller energy” of Refs. 19 and 20) is an energy scale characteristic of the electron-lattice coupling.

In the following we extract the nematic susceptibility $\chi_\varphi$ from our data using the above Landau theory. We use the approximation $C_{66}/C_{66,0} \approx Y_{110}/Y_0$, where $Y_0$ is the non-critical background. For $Y_0$, we use 33%Co-Ba122 data\cite{29}, the temperature-dependence of which can be very well described by the empirical Varshni-formula\cite{30}

$$Y_0 = c_0 - s/(\exp(t/T) - 1)$$  

with $s/c_0 = 0.0421$ and $t = 123.6$ K (see inset in Fig. 1(a)). $c_0/Y_{(293 \text{ K})}$ remains a free parameter, because we lack absolute values of $Y$. The values of $c_0/Y_{(293 \text{ K})}$ were adjusted in order to obtain good agreement with equation 4 for the underdoped samples and then linearly extrapolated to higher doping levels (see insets of Fig. 2). Making use of equation 3, the normalized nematic susceptibility $\frac{\lambda^2 \chi_\varphi}{C_{66,0}}$ can thus be obtained from our data and is shown in Fig. 2 for both electron- and hole-doped Ba122. We first discuss the doping dependence of the magnitude and then the detailed temperature dependence of $\chi_\varphi$.

Fig. 3(a) shows the magnitude of the nematic susceptibility $\chi_\varphi$ (in units of $\lambda^2/C_{66,0}$) as a color-coded map in the composition-temperature phase diagram of Co-Ba122 and K-Ba122. $\chi_\varphi$ is enhanced most strongly for the undoped compound right above $T_s$ and decreases smoothly with both electron and hole doping. A significant enhancement of $\chi_\varphi$ occurs in a broad band around the structurally distorted phase, as expected. Importantly, $\chi_\varphi$ is still enhanced in the overdoped region, where there is no structural phase transition. In fact, there appears to be a universal relationship between the ratio

FIG. 2. (color online). Normalized nematic susceptibility, $\chi_\varphi/C_{66,0}$, obtained from the critical part of the Young’s modulus of (a) Co-Ba122 and (b) K-Ba122. Dashed lines correspond to a Curie-Weiss fit. Insets show the parameter $c_0/Y_{110}(293 \text{ K})$ used for separating the critical part from the background. Triangles mark the inflection point $T^*$ (see text).

FIG. 3. (color online). (a) Temperature and doping dependence of the magnitude of $\lambda^2 \chi_\varphi/C_{66,0}$ for both Co-Ba122 and K-Ba122. (b) $T_s/T_{s,max}$ as a function of the maximum value of $\chi_\varphi/C_{66,0}$ for all overdoped samples. $T_{s,max} = 25 \text{ K} (38 \text{ K})$ for Co-Ba122 (K-Ba122). (c) Phase diagram showing the doping dependence of $T^*$ (triangles), $T_{s,CW}^*$ (diamonds) and $T_s$ (squares). The red dashed area corresponds to the “critical” region where $\chi_\varphi(T)$ diverges. (d) Doping dependence of $T_{s,CW}^* - T_0 = \frac{\lambda^2}{AC_{66,0}}$ (see text). All lines are guides to the eye.
$T_c/T_{c,max}$ and the maximum value of $\chi_\varphi(T)$ for all overdoped samples (Fig. 3(b)). This suggests a close tie between the nematic susceptibility and the occurrence of superconductivity for both electron- and hole-doped Ba122 systems. In this picture, the nematic susceptibility is taken as a measure of the strength of nematic fluctuations which mediate superconducting pairing. We note that the monotonic decrease of $\chi_\varphi$ with doping is at variance with results of Chu et al. [15], who reported a maximum of the nematic susceptibility around optimal doping from measurements of the strain-derivative of the resistivity anisotropy in Co-Ba122.

The dashed lines in Fig. 3(a) show a fit of the data to equation 4, which takes the form $\lambda^2x_\varphi(T) = T_{c0}^{CW} - T_0$. Such a fit works well for both under- and overdoped Co-Ba122, but only for underdoped K-Ba122. The resulting parameters are plotted in Fig. 3(c),(d). $T_c^{CW}$ closely follows $T_s$ and the coupling energy $T_{c0}^{CW} - T_0 \propto \lambda^2$ is practically doping independent. In the electron-doped system, $T_c^{CW}$ changes sign smoothly around optimal doping and overdoped samples also show critical softening. Both of these behaviors are suggestive of a quantum critical point near optimal doping, as has been shown in an essentially equivalent analysis in Ref. [20] for Co-Ba122. For K-Ba122, in contrast, only samples that actually undergo the structural transition ($x \leq 24\%$K) show critical softening, while for the other samples ($x \geq 30\%$K) the critical softening is cut off at $T \gtrsim 75$ K and the Curie-Weiss law is no longer followed.

A lower limit for the temperature at which the Curie-Weiss law breaks down, $T^*$, is given by the maximum of the derivative of $\chi_\varphi(T)$ and has been marked in Fig. 3(a), (b) by open triangles and is also plotted in Fig. 3(c). As a function of doping, $T^*$ first decreases, closely following $T_s$, and then increases upon further doping. Fig. 3(c) clearly shows that the region of critical softening extends to near zero temperatures only in the electron-doped system, in agreement with a quantum critical scenario. Note that, in order to “look beneath” the superconducting dome, we used a 6%Co+2%Mn-codoped sample, because Mn substitution strongly suppresses $T_c$ but hardly affects $T_s$. On the hole-doped side, the values of $T^*$ do not go below $\sim 75$ K, which is incompatible with a quantum critical point. At low temperatures, our nematic susceptibility data rather suggest a first-order transition between the orthorhombic/magnetic and tetragonal ground states as a function of K-content. We point out that the above result is rather surprising in a scenario in which superconductivity arises due to the fluctuations surrounding a QCP, because here the system with the higher maximum $T_c$ (K-Ba122) exhibits less critical behavior.

Finally, we discuss the response of the nematic susceptibility below $T_c$. The high resolution of our data allows to resolve even small effects at high doping levels (see Fig. 4(a)). Near optimal doping, $Y_{110}/Y_0$ hardens significantly as a response to superconductivity, in agreement with previous reports [15-20]. We observe an additional, small step-like softening of the Young’s modulus at $T_c$ at intermediate doping levels ($x = 48 - 60 \%$K), which is surprisingly absent at 82% K. Highly overdoped samples ($x = 90 \%$K and $x = 12 \%$Co) exhibit only the step-like anomaly, which might however mask a tiny hardening below $T_c$, if existent. This step-like softening of $Y(T)$ at $T_c$ is actually the usual behavior expected from thermodynamics at a second order phase transition and is related to the stress-derivative of $T_c$, i.e. the normal coupling between superconductivity and the lattice [22]. The hardening, on the other hand, directly reflects the competition between superconductivity and the nematic order parameter $\varphi$ affecting the lattice via equation 3 [13-20]. In Fig. 4(b) the effect of this competition, as quantified by the discontinuous slope change of $Y/Y_0(T)$ at $T_c$ (ignoring the step-like anomaly), is plotted versus doping. For both Co-Ba122 and K-Ba122 the slope change is maximal near optimal doping and then decreases strongly for overdoped samples with a weak tail extending up to at least 82% K on the hole-doped side. The maximum value is three times larger for Co-Ba122 than for K-Ba122, suggesting that the coupling of the nematic order to superconductivity is significantly stronger in this system. Finally, we point out that e.g. the 60...
% K sample exhibits a broad hardening of $Y_{[110]}$ starting at $\sim 60$ K, which is clearly unrelated to the onset of superconductivity. To prove this, we show in Fig. 3(d) the bulk transitions of these samples as determined by thermal expansion, which are all quite sharp.

In conclusion, we have shown that the nematic susceptibility is enhanced over the whole superconducting regions in both K- and Co-doped Ba122, suggesting that fluctuations associated with the electronic nematic order may play a crucial role in superconducting pairing. On the other hand, nematic fluctuations exhibit quantum critical-like behavior only in Co-Ba122 and not in K-Ba122, which has the higher $T_c$. The latter compound also shows a much weaker response of nematic fluctuations to superconductivity. This naturally raises the question whether quantum criticality is really important for obtaining high $T_c$, and/or if nematic fluctuations are indeed directly involved in the pairing. Although from our measurements it is impossible to determine whether nematic order is driven by spin or orbital physics, we hope that our detailed data will stimulate further theoretical and experimental work aimed at clarifying the microscopic nature of the nematic state and its relationship to superconductivity.

Acknowledgements: We thank Andres Cano, Rafael M. Fernandes, Jörg Schmalian, Wilfried Schranz, Kees van der Beek, and Bernd Wolf for valuable discussions. This work was funded by the DFG through SPP1458 and via a “Feasibility Study of Young Scientists” in the framework of the Exzellenz-Initiative at the KIT.

\[\text{anna.boehmer@kit.edu}\]

[1] M. R. Norman, Science 332, 169 (2011).
[2] G. R. Stewart, Rev. Mod. Phys. 83, 1589 (2011).
[3] C.-C. Lee, W.-G. Yin, and W. Ku, Phys. Rev. Lett. 103, 267001 (2009).
[4] W. Lv, F. Krüger, and P. Phillips, Phys. Rev. B 82, 045125 (2010).
[5] H. Kontani, R. Saito, and S. Onari, Phys. Rev. B 84, 024528 (2011).
[6] S. Nandi, M. G. Kim, A. Kreyssig, R. M. Fernandes, D. K. Pratt, A. Thaler, N. Ni, S. L. Bud’ko, P. C. Canfield, J. Schmalian, R. J. McQueeney, and A. I. Goldman, Phys. Rev. Lett. 104, 057006 (2010).
[7] R. M. Fernandes and J. Schmalian, Supercond. Sci. Technol. 25, 084005 (2012).
[8] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
[9] H. Kontani and S. Onari, Phys. Rev. Lett. 104, 157001 (2010).
[10] K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, Phys. Rev. Lett. 101, 087004 (2008).
[11] I. I. Mazin and J. Schmalian, Physica C 469, 614 (2009).
[12] J.-H. Chu, J. G. Analytis, K. D. Greve, P. L. McMahon, Z. Islam, Y. Yamamoto, and I. R. Fisher, Science 39, 824 (2010).
[13] M. Yi, D. Lu, J.-H. Chu, J. G. Analytis, A. P. Sorini, A. F. Kemper, B. Moritz, S.-K. Mo, R. G. Morre, M. Hashimoto, W.-S. Lee, Z. Hussain, T. P. Devereaux, I. R. Fisher, and Z.-X. Shen, PNAS 208, 6878 (2011).
[14] S. Kasahara, H. J. Shi, K. Hashimoto, S. Tonegawa, Y. Mizukami, T. Shibauchi, K. Sugimoto, T. Fukuda, T. Terashima, A. H. Nevidomskyy, and Y. Matsuda, Nature 486, 382 (2012).
[15] J.-H. Chu, H.-H. Kuo, J. G. Analytis, and I. R. Fisher, Science 337, 710 (2012).
[16] S. A. K. E. Fradkin, M. J. Lawler, J. P. Eisenstein, and A. P. Mackenzie, Annu. Rev. Condens. Matter Phys. 1, 153 (2010).
[17] M. Vojta, Adv. Phys. 58, 699 (2009).
[18] R. M. Fernandes, L. H. VanBebber, S. Bhattacharya, P. Chandra, V. Keppens, D. Mandrus, M. A. McGuire, B. C. Sales, A. S. Sefat, and J. Schmalian, Phys. Rev. Lett. 105, 157003 (2010).
[19] T. Goto, R. Kurihara, K. Araki, K. Mitsumoto, M. Akatsu, Y. Nenmot, S. Tatematsu, and M. Sato, J. Phys. Soc. Jpn. 80, 073702 (2011).
[20] M. Yoshizawa, D. Kimura, T. Chiba, S. Simayi, Y. Nakanishi, K. Kihou, C.-H. Lee, A. Iyo, H. Eisaki, M. Nakajima, and S. Ushida, J. Phys. Soc. Jpn. 81, 024604 (2012).
[21] C. Meingast, B. Blank, H. Bürkle, B. Obst, T. Wolf, H. Wühl, V. Selvamanickam, and K. Salama, Phys. Rev. B 41, 11299 (1990).
[22] A. E. Böhm and et al. (unpublished).
[23] A. V. Kityk, T. P. Soprunyuk, A. Fith, W. Schranz, and H. Warhanke, Phys. Rev. B 73, 6337 (1996).
[24] W. Schranz, H. Kabelka, and A. Tröster, Ferroelectrics 426, 242 (2012).
[25] W. Schranz, H. Kabelka, A. Serras, and M. Burock, Appl. Phys. Lett. 101, 141913 (2012).
[26] M. Yoshizawa and S. Simayi, Modern Physics Letters B 26, 1230011 (2012).
[27] E. Salje, Phase transitions in ferroelastic and co-elastic crystals (Cambridge university press, 1990).
[28] A. Cano, M. Civelli, I. Eremin, and I. Paul, Phys. Rev. B 82, 024048 (2010).
[29] C. Meingast, F. Hardy, R. Heid, P. Adelmann, A. Böhmer, P. Burger, D. Ernst, R. Fromknecht, P. Schweiss, and T. Wolf, Phys. Rev. Lett. 108, 177004 (2012).
[30] Y. P. Varshni, Phys. Rev. B 2, 3952 (1970).
[31] 2% Mn content decreases $T_c$ equivalently to 0.7% Co substitution; currently unpublished.
[32] The value of the step-like softening agrees within a factor of 2 with estimations from specific-heat and thermal-expansion measurements via the Ehrenfest relationship for 48%, 60%, and 90% K-content and 12% Co-content.