Critical Slowing Down of Quadrupole and Hexadecapole Orderings in Iron Pnictide Superconductor

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Ultrasonic measurements have been carried out to investigate the critical dynamics of structural and superconducting transitions due to degenerate orbital bands in iron pnictide compounds with the formula Ba(Fe 1-xCo x)2As 2. The attenuation coefficient δ(110) of the longitudinal ultrasonic wave for (C 11 + C 12 + 2C 44)/2 for x = 0.036 reveals the critical slowing down of the relaxation time around the structural transition at T s = 65 K, which is caused by ferro-type ordering of the quadrupole O 2− yz associated to the strain ε 0 . The attenuation coefficient α 0 of the transverse ultrasonic wave for C 66 for x = 0.071 also exhibits the critical slowing down around the superconducting transition at T SC = 23 K, which is caused by ferro-type ordering of the hexadecapole H 66 (r, r) = O 2− yz(r)O 2− yz(r) + O 2− yz(r)O 2− yz(r) of the bound two-electron state coupled to the rotation α 0 . It is proposed that the hexadecapole ordering associated with the superconductivity brings about spontaneous rotation of the macroscopic superconducting state with respect to the host tetragonal lattice.

1. Introduction

Since the discovery of superconductivity in iron pnictide compounds with the formula LaFeAsO 1− yF y with a high transition temperature of T SC = 26 K by Hosono and his coworkers in 2008, 1, 2 many researchers have been involved in the search for various iron-based composites showing high superconducting transition temperatures and the inherent mechanism of the superconductivity. Among the many iron-based compounds, the family of LaFeAsO with the 1111-type ZrCuSiAs structure shows transition temperatures as high as T SC ~ 56 K. 2) The family of BaFe 2As 2 with the 122-type ThCr 2Si 2 structure exhibits superconductivity with T SC ~ 38 K upon the substitution of barium for potassium. 3) The other family of LiFeAs with the 111-type PbFCl structure shows superconductivity with T SC ~ 18 K, 4) and FeSe with the 11-type PbO structure shows superconductivity with T SC ~ 10 K. 5) These compounds have a common lattice structure with a two-dimensional square of iron layers, which gives the electronic band structure due to 3d orbitals of Fe 2+ ions favorable for achieving superconductivity with high transition temperatures.

The 122-type compounds of BaFe 2As 2 showing the superconductivity under either chemical doping or applying pressure have received particular attention, 6–8) because high-quality single crystals with a fair size are available for experiments. The end material of BaFe 2As 2 exhibits a structural phase transition from the tetragonal phase with space group D 4h 3 (I4/mmm) to the orthorhombic phase with space group D 2h 3 (Fmmm) simultaneously accompanied by antiferro-magnetic ordering with a stripe-type spin structure at transition temperatures of T s = T N = 140 K. 3, 9–10) The chemical doping by substituting Co ions with 3d f electrons for Fe ions with 3d g electrons in Ba(Fe 1− xCo x) 2As 2 reduces both the structural and antiferro-magnetic transition temperatures while slightly splitting the two transition temperatures so that T s > T N. 11–14) The Co-ion doped compounds with x > 0.03 reveal the superconductivity below the successive structural and magnetic transitions. With increasing the Co dopant concentration x to the quantum critical point (QCP) of x QCP = 0.061, the structural and antiferro-magnetic orderings disappear and the superconducting phase manifests itself. Upon further doping over x QCP, the optimized superconducting transition temperature of as high as T SC = 23 K emerges in the compound with x = 0.071.

In order to clarify the interplay of the structural transition to the superconductivity in the iron pnictide Ba(Fe 1− xCo x) 2As 2, the softening of the elastic constant C 66 as a precursor of the structural transition has been intensively investigated. By using resonance ultrasonic spectroscopy, Fernandez et al. first showed the softening of C 66 in Ba(Fe 1− xCo x) 2As 2 for the end material and the over-doped compounds with x = 0.08, the latter exhibiting a superconducting transition at T SC = 16 K, and proposed that the softening of C 66 is caused by spin nematic fluctuations of the Fe 3d f electrons. 15) By using the ultrasonic pulse-echo method, Goto et al. showed the softening of C 66 by 21% for x = 0.071 from 300 K down to the optimized superconducting transition temperature T SC = 23 K, and deduced that the electric quadrupole O 2− yz associated with the degenerate y z and x′ z′ orbitals of the Fe 3d f ion coupled to the elastic strain ε 0 of the transverse ultrasonic wave plays a role in the appearance of the superconductivity. 16) Here, the x and y (x′ and y′) coordinates for neighboring Ba-Ba (Fe-Fe) directions
are adopted. Yoshizawa et al. systematically investigated the elastic constant $C_{66}$ for compounds with various Co concentrations and clarified the quantum criticality of the softening of $C_{66}$ around the QCP of $\Delta x_{\text{QCP}} = 0.061$.\textsuperscript{17}

Angle-resolved photoemission spectroscopy experiments on Ba$_{0.8}$K$_{0.2}$Fe$_2$As$_2$,\textsuperscript{18} muon resonance experiments on Ba$_{1-x}$K$_x$Fe$_2$As$_2$,\textsuperscript{39} microwave penetration depth measurements of PrFe$_2$AsO$_{x}$,\textsuperscript{20} and NMR relaxation rate measurements of LiFe$_{1-x}$M$_x$AsO$_{1-x}$Fe$_2$ commonly show mostly isotropic and nodeless superconducting energy gaps with an s-like shape. The robustness of the superconducting transition temperature $T_{\text{SC}}$ for nonmagnetic impurity doping to the system is favorable for the sign-conserving s-wave state of $s_{\pm}$.\textsuperscript{21–23} Taking the quadrupole fluctuations associated with the elastic softening of $C_{66}$ into account, the $s_{\pm}$ state for the superconducting energy gap has been theoretically deduced.\textsuperscript{24–26} On the other hand, neutron scattering experiments on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ have shown a magnetic excitation peak around $q = (1/2, 1/2, 1)$, indicating a role of the antiferro-magnetic fluctuations in the superconductivity.\textsuperscript{27} Accordingly, the sign-reversing $s_{\pm}$-wave state has been presented while emphasizing the spin fluctuation effects due to the antiferro-magnetic interaction.\textsuperscript{28–30} The clarification of the superconducting mechanism of the iron pnictides is still an important issue in solid-state physics.

Since ultrasonic waves with frequencies as high as 100 MHz easily penetrate into metals, attenuation measurements are useful for examining order parameter dynamics around phase transitions in metals. There are a few reports on ultrasonic attenuation measurements around the structural and superconducting transitions of the iron pnictides.\textsuperscript{31,32} However, the attenuation of ultrasonic waves relating the elastic constant $C_{66}$ has not been reported so far to the best of our knowledge. In the present paper, we show the critical dynamical behavior around the QCP of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and the critical divergence of the attenuation of ultrasonic waves along the structural and superconducting transitions. In order to avoid applying undesired stress to the samples, we carefully kept each sample in a brass disk during the ultrasonic experiments. A vector-type detector based on the ultrasonic pulse-echo method was used for simultaneous measurements of the attenuation coefficient $\alpha$ and velocity $v$. A $^3$He cryostat (Oxford Heliox TL) was employed for the ultrasonic measurements down to 250 mK.

3. Results

3.1 Attenuation around superconducting transition for $x = 0.071$

In order to investigate the dynamical features of the superconducting transition while clearly distinguishing them from the structural and antiferro-magnetic orderings, we focused on the over-doped compound $x = 0.071$, which exhibits the optimized superconducting transition temperature $T_{\text{SC}} = 23$ K but neither a structural transition nor antiferro-magnetic ordering. We measured the attenuation coefficient $\alpha_{66}$ using the transverse ultrasonic waves with the propagation vector $q/[100]$ and polarization vector $\mathbf{E} /[010]$ with frequencies of 119, 167, and 215 MHz. The attenuation coefficient $\alpha_{66}$ for $x = 0.071$ in Fig. 1(a) increases with decreasing temperature below 80 K in the normal phase and reveals critical divergence with approaching the superconducting transition point of $T_{\text{SC}} = 23$ K. With further lowering the temperature below $T_{\text{SC}} = 23$ K, the attenuation coefficient $\alpha_{66}$ rapidly decreases. In both the normal and superconducting phases, the frequency dependence of the attenuation coefficient $\alpha_{66}$ obeys the $\omega^2$ law, consistent with the low-frequency regime of the Debye formula.

The elastic constant $C_{66}$ in the normal phase for $x = 0.071$ exhibits the softening, which is again shown in Fig. 1(a).\textsuperscript{16} This softening is caused by the interaction of the quadrupole $O_{x^2-y^2}$ to the strain $\varepsilon_{xy}$ expressed as

$$H_{\text{QS}} = -g_{\alpha_{66}}O_{x^2-y^2}\varepsilon_{xy}. \quad (1)$$
Here, $g_{c'z'-y''}^2$ is the quadrupole-strain coupling constant. We expect the Curie-type behavior of the susceptibility proportional to the reciprocal temperature as $\chi_Q = (\langle \phi | O_{c'z'-y''} | \phi \rangle |^2 / T$ for suffixes $l = y'z'$ and $z'x'$ of the degenerate orbitals. The softening of $C_{66}$ in the normal phase is written by $^{34}$

$$C_{66} = C_{66}^0 - \frac{n_0 g_{c'z'-y''}^2 \chi_Q}{1 - g_{c'z'-y''}^2 \chi_Q} = C_{66}^0 \left( \frac{T - T_0^Q}{T - \Theta_Q} \right).$$  \(2\)

Here, $C_{66}^0$ is the background elastic constant when softening is absent and $g_{c'z'-y''}^2$ is the mutual interaction coefficient between the quadrupoles $O_{c'z'-y''}$ at different sites. The solid line in Fig. 1(a) is the softening of $C_{66}$ fit by Eq. (2) in the normal phase. We obtain negative values of the quadrupole interaction energy $\Theta_Q = -47.0$ K and the critical temperature $T_0^Q = \Theta_Q + 40 = 26.5$ K. This fitting gives the quadrupole-strain interaction energy $40 = 20.5$ K, which represents the coupling energy between the quadrupoles at different sites mediated by the strain $\varepsilon_{xx}$.

The negative quadrupole interaction energy $\Theta_Q = -47.0$ K indicates the antiferro-type quadrupole interaction for $x = 0.071$. The negative critical temperature of $T_0^Q = -26.5$ K corresponds to the fictitious critical temperature of the structural instability for $C_{66} \to 0$. Consequently, the superconducting transition temperature $T_{SC}$ is definitely distinguished from the fictitious critical temperature $T_0^Q = -26.5$ K. We conclude that the marked increase in the attenuation coefficient $\alpha_{66}$ for $x = 0.071$ in Fig. 1(a) is caused by the critical slowing down of the order parameter around the superconducting transition, which is strictly distinguished from the quadrupole $O_{c'z'-y''}$ interacting to the strain $\varepsilon_{xx}$ in Eq. (1).

Because two electrons are accommodated in the degenerate $y'z'$ and $z'x'$ orbitals of an Fe$^{2+}$ ion, we tentatively adopt $n_Q = 2N_{Fe} = 3.92 \times 10^{22}$ cm$^{-3}$ in Eq. (2) as the maximum number of electrons, that play a role in the softening of $C_{66}$. Here, $N_{Fe}$ is the number of Fe$^{2+}$ ions per unit volume. The solid line in Fig. 1(a) for the softening of $C_{66}$ fit by Eq. (2) gives the quadrupole-strain coupling constant $g_{c'z'-y''}^2 = 1045$ K per electron. This coupling constant is comparable with the results for manganese compounds of $g = 1167$ K for La$_{0.88}$Sr$_{0.12}$MnO$_3$ and $g = 1020$ K for Pr$_{0.65}Co_{0.35}$MnO$_3$ with considerably extended 3d orbitals.~$^{35,36}$ but is considerably larger than $g \sim 100$ K for rare-earth compounds of the form RBs with well-screened 4f orbitals in the inner shell.~$^{37}$

In our attempt to clarify the order parameter dynamics around the superconducting transition, we analyzed the frequency dependence of the attenuation coefficient $\alpha_{66}$ in Fig. 1(a) in terms of the Debye formula expressed as

$$\alpha_{66} = \frac{C_{66}^0(\Theta_{Q}) - C_{66}(0)}{2\rho \nu_{66}(\Theta_{Q})} \omega^2 \tau \frac{1}{1 + \omega^2 \tau^2}. \quad (3)$$

Here, $C_{66}(\Theta_{Q})$ and $C_{66}(0)$ stand for the high- and low-frequency limits of the elastic constant $C_{66}$, respectively. We regard the elastic constant experimentally observed in Fig. 1(a) as the low-frequency limit $C_{66}(0)$ in Eq. (3). The background $C_{66}^0$ used in the analysis based on the quadrupole susceptibility of Eq. (2) corresponds to the high-frequency limit of the elastic constant $C_{66}(\Theta_{Q})$ for the sound velocity $v_{66}(\Theta_{Q}) = \sqrt{C_{66}(\Theta_{Q})/\rho_{M}}$ in Eq. (3).~$^{10}$ $\nu_{Q} = (\langle \phi | O_{c'z'-y''} | \phi \rangle |^2 / T$ is the angular frequency of the employed ultrasonic waves, and $\tau$ is the relaxation time of the order parameter fluctuation of the system. We show the temperature dependence of the relaxation rate $\tau$ obtained by Eq. (3) in Fig. 1(b) and that of the relaxation rate $\tau^{-1}$ in the inset of Fig. 1(b). The rapid increase in the relaxation rate $\tau$ around $T_{SC} = 23$ K indeed indicates the critical slowing down of the order parameter accompanying the superconducting transition in the system.

The correlation length $\xi$ of the order parameter $Q(r)$ for an appropriate phase transition is widely used to describe the correlation function as $G(r) = \langle Q(r) Q(0) \rangle \propto r^{-d-\xi} e^{-r/\xi}$. Here, $|r| = r$ stands for the spatial distance between the order parameters and $d$ denotes the dimension of the system. In the vicinity of the critical temperature $T_0^Q$ of the phase transition, the correlation length $\xi$ becomes infinite due to the increase in the local order as $\xi = \xi(0) r^{-d}$ for a reduced temperature of $\varepsilon = (T - T_0^Q)/T_0^Q$. The critical index $\nu = 1/2$ is expected from mean field theory.~$^{38}$

When an ultrasonic pulse wave enters a crystal, the equilibrium state of the system is instantaneously perturbed to a nonequilibrium state. After the relaxation time $\tau$, the system returns to the equilibrium state. In the vicinity of the critical
point, however, the relaxation time $\tau$ becomes infinite due to the divergence of the correlation length as $\tau \propto \xi^z$ for dynamical critical index $z$. Presumably, the critical slowing down of the relaxation time $\tau$ is explained by the critical index $z\nu$ as $^{39-42}$

$$\tau = \tau_0 \frac{T - T_0^0}{T_0^0}^{-z\nu} = \tau_0 e^{-z\nu}.$$  \hspace{1cm} (4)

In mean field theory, the dynamical critical index $z = 2$ is expected. Actually, the temperature dependence of the relaxation time $\tau$ in the normal phase of Fig. 1(b) is well reproduced by the solid line for the critical index $z\nu = 1$, the critical temperature $T_0^0 = 23.0$ K, and the attempt time $\tau_0^0 = 6.0 \times 10^{-11}$ s. In the superconducting phase, however, we obtain $z\nu = 1/3$, $T_0^s = 23.5$ K, and $\tau_0^s = 5.8 \times 10^{-11}$ s. The distinct deviation of the critical index of $z\nu = 1/3$ from $z\nu = 1$ of mean field theory may be caused by the inherent property that the hexadecapole ordering appears in accordance with the superconductivity in the present iron pnictide. The analysis of the experimental results in Fig. 1(b) gives a ratio of the attempt times of $\tau_0^s / \tau_0^0 = 1.03$, which is distinguished from the ratio of $\tau_0^s / \tau_0^0 = 2$ expected from mean field theory. Because the ultrasonic echo signal almost disappears in the vicinity of the superconducting transition point due to the critical slowing down, the absolute values of the attenuation coefficients inevitably include experimental errors.

### 3.2 Attenuation around structural transition for $x = 0.036$

Next, we examine the critical slowing down around the structural transition from the tetragonal to orthorhombic phases of the under-doped compound $x = 0.036$. This is worth comparing with the critical slowing down around the superconducting transition of the over-doped compound $x = 0.071$ presented in Sect. 3.1.

The temperature dependence of the elastic constants for $x = 0.036$ is shown in Fig. 2. We denote the propagation vector as $q$ and the polarization vector as $\xi$ for the ultrasonic waves measured in Fig. 2. The elastic constant $C_{66}$ in Fig. 2(e) measured by the transverse ultrasonic wave reveals considerable softening of 85% with decreasing temperature from 300 K down to the structural transition temperature of $T_s = 65$ K. As indicated by arrows in Fig. 2(e), the antiferromagnetic ordering at $T_N = 39$ K and the superconducting transition at $T_{SC} = 16.4$ K are also observed as anomalies in $C_{66}$. The softening of $C_{66}$ in the tetragonal phase is reproduced by the solid line in Fig. 2(e), which is obtained by Eq. (2) for the quadrupole interaction energy of $\Theta_Q = 47$ K, the quadrupole-strain interaction energy $\Delta_Q = 16$ K, and the critical temperature of $T_0^s = \Theta_Q + \Delta_Q = 63$ K. The background of $C_{66} = 2.87 \times 10^{10}$ J/m$^3$ is shown by the dashed line in Fig. 2(e). The critical temperature $T_0^s = 63$ K is in agreement with the experimentally observed structural transition temperature $T_s = 65$ K. We deduce the quadrupole-strain coupling constant to be $g_{q} e^{\nu s} = 920$ K per electron by adopting the electron number $N_{q} = 2N_{q} p$ in Eq. (2). The positive values of the quadrupole interaction energy $\Theta_Q = 47$ K and the temperature $T_0^s = 63$ K are consistent with the ferro-quadrupole ordering $O(6)_{c-q}^{\nu s}$ accompanying the structural transition from the tetragonal to orthorhombic phase.

The elastic constant $C_{L[110]} = (C_{11} + C_{12} + 2C_{66})/2$ in Fig. 2(d) measured by a longitudinal ultrasonic wave with the propagation direction $q// [110]$ parallel to the polarization direction $\xi$ also shows marked softening with decreasing temperature down to the structural transition at $T_s = 65$ K. With further decreasing temperature in the distorted orthorhombic phase, the graph of the elastic constant $C_{L[110]}$ slightly bends at the antiferromagnetic transition temperature $T_N = 39$ K and distinctly decreases at the superconducting transition temperature $T_{SC} = 16.4$ K. The longitudinal ultrasonic wave for $C_{L[110]}$ induces elastic strain of $e_{q_{110}} = e_B / 3 - e_{\alpha} / (2\sqrt{3}) + e_{\alpha y}$.

The coupling of the strain $e_{\alpha y}$ to the quadrupole $O(6)^{\nu s}$ induces the softening in $C_{L[110]}$, partly consisting of $C_{66}$. The volume strain $e_B = e_{\alpha x} + e_{\alpha y} + e_{\alpha z}$ and the tetragonal strain $e_{\alpha} = (2e_{\alpha x} - e_{\alpha x} - e_{\alpha y}) / \sqrt{3}$ scarcely affect the softening.

We initially attempted to measure the attenuation coefficient $\alpha_{66}$ by using the pure transverse ultrasonic wave. However, the attenuation of $\alpha_{66}$ near the structural transition was too large to measure. In the present experiments, therefore,
we used the longitudinal ultrasonic wave, which shows relatively moderate damping, to measure the attenuation coefficient $\alpha_{L[110]}$. In Fig. 3(a), we show the attenuation coefficient $\alpha_{L[110]}$ for $x = 0.036$ acquired using longitudinal ultrasonic waves with frequencies of 112, 186, and 260 MHz together with the elastic constant $C_{L[110]}$. The attenuation coefficient $\alpha_{L[110]}$ increases considerably with approaching the structural transition point of $T_s = 65$ K from both sides. With decreasing temperature in the orthorhombic phase, the attenuation $\alpha_{L[110]}$ exhibits a distinct peak at the superconducting transition point of $T_{SC} = 16.4$ K. The missing ultrasonic echo signal due to considerable damping of the longitudinal ultrasonic wave prevents us from acquiring $\alpha_{L[110]}$ approaching the structural transition. Nevertheless, the distinct tendency of the divergence of $\alpha_{L[110]}$ around the structural transition at $T_s = 65$ K indicates the critical slowing down of the relaxation time $\tau$ for the order parameter fluctuation.

The frequency dependence for $\alpha_{L[110]}$ for the under-doped compound $x = 0.036$ in Fig. 3(a) is analyzed in terms of the Debye formula in Eq. (3), where we read the attenuation as $\alpha_{L[110]}$ and the elastic constant as $C_{L[110]}$. We depict the temperature dependence of the relaxation time $\tau$ in Fig. 3(b) and the relaxation rate $\tau^{-1}$ in the inset of Fig. 3(b). The increase in the relaxation time $\tau$ around the structural transition at $T_s = 65$ K is caused by the critical slowing down of the quadrupole $O_{x^2-y^2}$, which is the order parameter of the structural transition. The ultrasonic frequencies of $\omega/2\pi$ up to 260 MHz used in the present experiments are much higher than the relaxation rate $\tau^{-1} < 100$ MHz in the vicinity of the structural transition point $T_s$ for the narrow reduced temperature region of $\epsilon = (T - T_0)/T_0 < 0.38$. As a result, the ultrasonic echo signal disappears on both sides around the structural transition point of $T_s = 65$ K as depicted in Fig. 3(a). The solid lines in Fig. 3(b) are fits for the relaxation time $\tau$ in terms of Eq. (4). Supposing that the critical temperature $T_0^c = 65$ K coincides with the structural transition point and the critical indices for both phases are consistent with $\nu = 1$ of mean field theory, we obtain the fit shown by the solid line in Fig. 3(b) using Eq. (4). This gives the attempt time $\tau^*_0 = 0.380 \times 10^{-9}$ s for the tetragonal phase and $\tau^*_0 = 1.15 \times 10^{-9}$ s for the orthorhombic phase.

The quadrupole-strain interaction of Eq. (1) induces the ferro-quadrupole ordering accompanying the structural transition. It is expected that the long-range Coulomb force between electrons bearing the quadrupole exhibits critical phenomena described by mean field theory. Actually, the adoption of the critical index $\nu = 1$ for both tetragonal and orthorhombic phases consistent with mean field theory reproduces the experimental results in Fig. 3. The small-echo signal due to the considerable damping of the longitudinal ultrasonic waves gives inevitable errors in the absolute-value of the attenuation coefficient $\alpha_{L[110]}$ in Fig. 3. The dispersive scattering of the ultrasonic wave by the domain wall due to the orthorhombic distortion is also included in the attenuation. These ambiguity might have resulted in the deviation of the experimentally determined ratio of $\tau^*_0/\tau_0 = 0.33$ from $\tau^*_0/\tau_0 = 2$ expected from mean field theory. The attempt time $\tau^*_0 = 0.55 \times 10^{-9}$ s of the structural transition for $x = 0.036$ in Fig. 3(b) is one order of magnitude larger than the attempt time $\tau^*_0 = 6.0 \times 10^{-11}$ s of the superconducting transition for $x = 0.071$ in Fig. 1(b). This notable result suggests that the order parameter showing the critical slowing down around the superconducting transition for $x = 0.071$ is distinguished from the ferro-quadrupole ordering accompanying the structural transition for $x = 0.036$.

3.3 Critical temperatures of the system

The ultrasonic measurements of the critical divergence in the attenuation coefficients and the softening in the elastic constants provided us with the critical temperatures, which characterize the structural and superconducting transitions of the present iron pnictide Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. In Fig. 4, we plot the critical temperatures obtained by the experimental results for $x = 0.036$ and 0.071 together with those for $x = 0.017$ and the end material $x = 0.43$.

The softening of the elastic constant $C_{66}$ analyzed by the quadrupole susceptibility $\chi_Q$ in Eq. (2) for $O_{x^2-y^2}$ gives the critical temperature $T^c_0 = \Theta_Q + \Delta_0$ corresponding to the structural instability point as $C_{66} \to 0$. As shown by blue closed circles and the blue solid line in Fig. 4, the critical temperature of $T^c_0 = 135$ K of the end material $x = 0$ decreases to $T^c_0 = 100$ K for $x = 0.017$ and $T^c_0 = 63$ K for $x = 0.36$. Beyond the QCP of $x_{QCP} = 0.061$, the critical temperature changes its sign to $T^c_0 = -26.5$ K for $x = 0.071$. The quadrupole interaction energy $\Theta_Q$ shown by red closed circles and the red solid line decreases from $\Theta_Q = 115$ K for the end
material \( x = 0 \) to \( \Theta_Q = 80 \) K for \( x = 0.017 \), \( \Theta_Q = 47 \) K for \( x = 0.036 \), and changes to a negative value of \( \Theta_Q = -47 \) K for \( x = 0.071 \). On the other hand, the quadrupole-strain interaction energy \( \Delta Q \) determined by the relaxation time \( \tau \) is shown by green solid circles and the green solid line remains at the positive value \( \Delta Q \sim 20 \) K. The positive critical temperatures \( T_s^0 \) of the under-doped compounds are comparable with the ferro-quadrupole ordering \( O_{\nu_{s,y}} \) associated with the structural transition from the tetragonal to orthorhombic phase, while the negative critical temperature \( T_s^0 \) for the over-doped compound \( x = 0.071 \), suggesting absence of the ferro-quadrupole ordering, implies the fictitious lattice instability point.

The infinite divergence of the relaxation time \( \tau \) due to the critical slowing down provides the critical temperature \( T_s^0 \) at which the long-range ordering appears due to freezing of the order parameter fluctuation.\(^{41,42}\) In the case of the structural transition for \( x = 0.036 \), the divergence of the relaxation time \( \tau \) with the critical temperature \( T_s^0 = 65 \) K, coincides with the structural transition temperature \( T_s = 65 \) K experimentally observed, and is in agreement with the critical temperature \( T_s^0 = \Theta_Q + \Delta Q = 63 \) K obtained by fitting the elastic softening of \( C_{66} \) by Eq. (2). This result confirms that the critical divergence of the ultrasonic attenuation coefficient \( \alpha_s \)\(^{110}\) for \( x = 0.036 \) is caused by the critical slowing down of the ferro-quadrupole order parameter \( Q_{s,y} \). The critical temperature for \( T_s^0 = 65 \) K for \( x = 0.036 \) is shown in Fig. 4 by a purple closed asterisk together with the critical temperature of \( T_s^0 = 63 \) K. Note that the quadrupole-strain interaction energy \( \Delta Q \sim 20 \) K, which is almost independent of the Co concentration, also promotes the appearance of the structural transition at the critical temperature \( T_s^0 = \Theta_Q + \Delta Q \). The quadrupole-strain interaction energy \( \Delta Q \) is shown by green closed circles in Fig. 4.

In the case of the superconducting transition for \( x = 0.071 \), the critical temperature \( T_s^0 = 23 \) K determined by the critical slowing down of the relaxation time \( \tau \) is in good agreement with the superconducting transition temperature \( T_{SC} = 23 \) K. In Fig. 4, we show the former critical temperature \( T_s^0 = 23 \) K for the relaxation time \( \tau \) by a purple closed asterisk together with the latter superconducting transition temperature \( T_{SC} = 23 \) K by a black open square. The critical temperature \( T_s^0 = -26.5 \) K indicated by a blue filled circle corresponds to the fictitious lattice instability point as \( C_{66} \rightarrow 0 \). The fictitious instability point of \( T_s^0 = -26.5 \) K is definitely distinguished from the critical temperature \( T_s^0 = 23 \) K of the relaxation time \( \tau \) coinciding with the superconducting transition temperature \( T_{SC} \). This result evidences that the order parameter exhibiting the critical slowing down around the superconducting transition does not correspond to the electric quadrupole \( O_{\nu_{s,y}} \) but to other quantum degrees of freedom, which interact with the transverse ultrasonic waves used in the experiments. It is of great importance to identify the order parameter, which brings about the critical slowing down of the relaxation time \( \tau \) around the superconducting transition. In Sect. 4.6, we give the electric hexadecapole carried by a two-electron state as a plausible order parameter associated with the superconducting transition.

4. Theory

4.1 Transverse acoustic wave

The relaxation time \( \tau \) determined by the ultrasonic attenuation reveals the critical slowing down around the superconducting transition for the compound \( x = 0.071 \) as well as the structural transition for \( x = 0.036 \). In our attempt to properly explain the ultrasonic experiments, we treat the couplings between the ultrasonic waves and electrons accommodated in the degenerate \( y'z \) and \( z'x \) orbitals of Fe ion. We will show plausible order parameters associated with the superconducting phase and the structurally distorted phase in the system.

The transverse ultrasonic wave with the propagation vector \( q = (q_x, 0, 0) \) and the polarization vector \( \mathbf{\xi} = (0, \xi_y, 0) \) employed in the present experiments is expressed in terms of the plane wave as

\[
\xi_y = \xi_y^0 \exp [i(q_x x - \omega t)].
\]

Here, \( \xi_y^0 \) is the amplitude of the ultrasonic wave, \( q_x \) is the wavevector component, and \( \omega \) is the angular frequency. The elastic constant is determined by the sound velocity \( v_s = \omega/q_x = v_{66} \) as \( C_{66} = \rho v_s^2 \). The transverse ultrasonic wave induces the deformation tensor

\[
\frac{\partial \xi_y}{\partial x} = i q_x \xi_y^0 \exp [i(q_x x - \omega t)] = i q_x \xi_y.
\]

The deformation tensor of Eq. (6) associated with the trans-
verse ultrasonic wave consists of the strain $\varepsilon_{xy}$ expressed as a symmetric tensor and the rotation $\omega_{xy}$ as an antisymmetric tensor

$$
\begin{aligned}
\left\{ \begin{array}{l}
\varepsilon_{xy} \\
\omega_{xy}
\end{array} \right\} = \frac{1}{2} \begin{pmatrix}
\frac{\partial \xi_y}{\partial x} & -\frac{\partial \xi_x}{\partial y} \\
\frac{\partial \xi_x}{\partial y} & \frac{\partial \xi_y}{\partial x}
\end{pmatrix}.
\end{aligned}
$$

In experiments using the transverse ultrasonic wave with $q = (q_x, 0, 0)$ and $\xi = (0, \xi_y, 0)$, we tune the perturbation parameter of $\delta = q_q \varepsilon_q^\theta = \omega/(\langle v \rangle_b \varepsilon_q^\theta) = (2\pi/\lambda_b \varepsilon_q^\theta)$ to an infinitesimal value by controlling the amplitude of the generated ultrasonic wave $\varepsilon_q^\theta$ and the frequency $\omega$ for a given phase velocity $v_s = v_0 s$. The rotation $\omega_{xy} = q_q \xi_q^\theta = \sin \theta$ and the strain $\varepsilon_{xy} = q_q \xi_q^\theta = \sin \theta$ are caused by slight twisting of the $x$- and $y$-axes by an angle of $\pi/2 + 2\theta$. This will later be illustrated in Figs. 7(a) and 7(b). The transverse ultrasonic wave simultaneously induces the rotation $\omega_{xy}$ and strain $\varepsilon_{xy}$, which are strictly distinguished from each other from a symmetrical viewpoint. Concerning the space group $D_{4h}$, the rotation $\omega_{xy}$ is compatible with $A_2$ symmetry, while the strain $\varepsilon_{xy}$ is compatible with $B_4^{42}$ symmetry. Thus, it is expected that the rotation $\omega_{xy}$ and strain $\varepsilon_{xy}$ interact with the electronic states of the system in different manners. When the electron-phonon interaction is absent, both the rotation $\omega_{xy}$ and strain $\varepsilon_{xy}$ propagate in the lattice with the same velocity $v_{0s}$.

In our attempt to explain the critical divergence of the ultrasonic attenuation coefficients and the marked elastic softening, we suppose that the interactions of thermally excited transverse acoustic phonons with electronic states play a role in the appearance of the structural and superconducting transitions. In the interactions of the transverse acoustic phonons with the electronic states of the iron pnictide, we take the Hamiltonian for the harmonic oscillators with polarization vectors in the $xy$ plane as

$$
H_{ph} = \sum_{q} \hbar \omega_q(q) \left( a^\dagger_{q,r} a_{q,r} + \frac{1}{2} \right)
+ \hbar \omega_q(q) \left( a^\dagger_{q,t} a_{q,t} + \frac{1}{2} \right).
$$

Here, $a_{q,r}$ and $a^\dagger_{q,r}$ respectively denote annihilation and creation operators of the transverse acoustic phonons with the polarization direction $\xi_r$ for $i = x$ and $y$ and momentum $\hbar q$. $\hbar \omega_q(q)$ stands for the phonon energy. The strain $\varepsilon_{xy}(r, t)$ and rotation $\omega_{xy}(r, t)$ at position $r$ and time $t$ are expressed in terms of the phonon operators $a_{q,r}$ and $a^\dagger_{q,r}$ as

$$
\begin{aligned}
\left\{ \begin{array}{l}
\varepsilon_{xy}(r, t) \\
\omega_{xy}(r, t)
\end{array} \right\} = \frac{1}{2} \begin{pmatrix}
\frac{\partial \xi_y}{\partial x} & -\frac{\partial \xi_x}{\partial y} \\
\frac{\partial \xi_x}{\partial y} & \frac{\partial \xi_y}{\partial x}
\end{pmatrix}
& \begin{pmatrix}
\frac{\partial \xi_y}{\partial x} \\
\frac{\partial \xi_x}{\partial y}
\end{pmatrix}
&+ \frac{1}{2} \begin{pmatrix}
\frac{\partial \xi_y}{\partial x} \\
\frac{\partial \xi_x}{\partial y}
\end{pmatrix}
\end{aligned}
$$

Here, $\rho_M$ is the mass density and $V$ is the volume of the system.

### 4.2 Degenerate $\psi_{yx}$ and $\psi_{zx}$ orbitals

Many reports of band-structure calculations on the iron pnictide compounds have shown inherent 3$d$ electronic structures favorable for the superconductivity as well as the structural transition.$^{46-50}$ Three sheets of hole surfaces with a cylinder-type structure exist around the $\Gamma$-point of the zone center and two electron pockets exist around the $X$-points of the zone boundary. We focus on the degenerate $y^z$ and $z^x$ bands occupied up to half filling, which are lifted by the transverse ultrasonic waves and acoustic phonons for $C_{66}$ with a small-wavenumber limit of $|q| \rightarrow 0$.

We show the electronic states of the degenerate $y'$ and $z$ orbitals in the crystalline electric field (CEF) Hamiltonian on an Fe$^{2+}$ ion with $D_{2d}$ site symmetry, which consists of an electric monopole, quadrupole, and hexadecapole expressed in terms of spherical harmonics as

$$
H_{CEF} = A_0^0 + A^2_2 \left( \frac{3\cos^2 \theta - 1}{2r^2} \right)
+ A^4_0 \left( \frac{35\cos^4 \theta - 30\cos^2 \theta + 3\cos^2 \theta}{8r^4} \right)
+ A^6_4 \left( \frac{3\sqrt{3} \sin^2 \theta - 6\cos^2 \theta + 2\sin^2 \theta}{r^4} \right).
$$

Here, $A_l^m$ denotes CEF parameters for the electric multipole potentials. The 3$d$ orbitals of the Fe$^{2+}$ ion in the CEF Hamiltonian of Eq. (10) splits into five orbital states with energy $E_{CEF}$ as

$$
E_{CEF} = \int dr \psi_{ry}(r) H_{CEF} \psi_{ry}(r).
$$

Here, $l$ denotes the 3$d$ orbital suffix. The point charge model of the CEF Hamiltonian gives the low-lying singlet states of $\psi_{3z^2-r^2}$ with $A_1$ symmetry and $\psi_{x^2-y^2}$ with $B_1$ symmetry and the mid-lying doublet state of $\psi_{y'}$ and $\psi_{z'}$ with $E$ symmetry and the excited singlet of $\psi_{y'}$ with $B_2$ symmetry.$^{53}$ Actually, the band calculations show that the three hole sheets around the $\Gamma$-point consist of the doublet state of $\psi_{y'}$ and $\psi_{z'}$ and the singlet state $\psi_{y'-z'}$.

In the present investigation, we suppose that the structural and superconducting transitions of the iron pnictide manifest themselves as a result of the spontaneous symmetry breaking associated with the degenerate $y'$ and $z$ bands, which are mapped on the special unitary group SU(2). In order to explore the quadrupole-strain interaction in the iron pnictide, we specially treat the degenerate $\psi_{y'}$ and $\psi_{z'}$ orbitals of the $E$ symmetry with half filling as

$$
\psi_{y'}(r) = -i \frac{f_{d}(r)}{\sqrt{2}} \left[ Y_2^1(\theta, \varphi) + Y_2^{-1}(\theta, \varphi) \right]
\psi_{z'}(r) = \frac{15}{4\pi} f_{d}(r) y'\frac{r^2}{r^2}.
$$

Here, the polar coordinate $(r, \theta, \varphi)$ represents the position vec-
tor $r = (x', y', z)$ of an electron. $f_2(r)$ is the radius function of a 3d electron, and $Y^j_{21}(\theta, \phi)$ is the spherical harmonics with angular momentum $l = 2$ and azimuthal quantum number $m = \pm 1$.

Since the direct product of the $E$ doublet is reduced as $E \otimes E = A_1 \oplus A_2 \oplus B_1 \oplus B_2$, we deduce that the degenerate $y'z$ and $zx'$ orbitals carry the electric quadrupoles $O_{2z^2-r^2} = (3x'^2 - r^2)/2r^2$ with $A_1$ symmetry, $O_{2y'y'}/r^2$ with $A_2$ symmetry, and $O_{x'y'y'} = \sqrt{3}(x'^2 - y'^2)/(2r^2)$ with $B_1$ symmetry and the angular momentum $l_z = -(i\partial/\partial y' - y'\partial/\partial x') = -i\partial/\partial \phi$ with $A_2$ symmetry. The quadrupole $O_{2y'y'}$ couples to the strain $\epsilon_{yz}$ of the transverse ultrasonic wave of $C_{6v}$, while $O_{2y'y'}$ couples to the strain $\epsilon_{y'y''}$ of the transverse ultrasonic wave of $(C_{11} - C_{12})/2$. The CEF Hamiltonian of Eq. (10) includes $O_{2z^2-r^2}$ with full symmetry.

Employing the identity matrix $\tau_0$ and the Pauli matrices $\tau_x$, $\tau_y$, and $\tau_z$ corresponding to the generator elements of the special unitary group SU(2), we present the quadrupoles $O_{2z^2-r^2}$, $O_{2y'y'}$, and $O_{x'y'y'}$ and the angular momentum $l_z$ in terms of the matrix for the orbital state $\psi_{yz}$ of Eq. (12) and $\psi_{x'y'}$ of Eq. (13) as

\[ O_{2z^2-r^2} = \frac{1}{r^2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \]

(14)

\[ O_{2y'y'} = \frac{\sqrt{3}}{r^2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \]

(15)

\[ l_z = -i \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = -\tau_y, \]

(16)

\[ O_{x'y'y'} = -\frac{\sqrt{3}}{r^2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = -\frac{\sqrt{3}}{r^2} \tau_z. \]

(17)

The Pauli matrices $\tau_x$, $\tau_y$, and $\tau_z$ obey the commutation relation

\[ [\tau_i, \tau_j] = 2i\epsilon_{ijk} \tau_k \quad (i, j, k = x, y, z). \]

(18)

Here, $\epsilon_{ijk}$ is the Levi-Civita symbol. As will be shown in Sects. 4.6 and 4.10, the commutation relation among the quadrupoles $O_{2y'y'}$ and $O_{x'y'y'}$ and the angular momentum $l_z$ of Eq. (18) brings about quantum fluctuations, which play a significant role in the manifestation of the specific superconductivity accompanying the hexadecapole ordering in the vicinity of the QCP.

The elastic strains $\epsilon_{yz}$ induced by the thermally excited transverse acoustic phonons or the experimentally generated transverse ultrasonic waves perturb the CEF Hamiltonian as

\[ H_{\text{CEF}}(r, \epsilon_{yz}) = H_{\text{CEF}}(r) + \sum_{T_y} \frac{\partial H_{\text{CEF}}(r)}{\partial \epsilon_{yz}}, \]

(19)

Because electrons accommodated in the degenerate $y'z$ and $zx'$ orbitals bear the electric quadrupoles, the second term of Eq. (19) proportional to the strain $\epsilon_{yz}$ is expressed in terms of the quadrupole-strain interaction as $^{30, 54}$

\[ H_{\text{QS}} = -g_{2z^2-r^2} O_{2z^2-r^2} \epsilon_{yz} - g_{2y'y'} O_{2y'y'} \epsilon_{y'y'y'}. \]

(20)

As the present ultrasonic experiments give a large coupling constant of $g_{2z^2-r^2} \approx 1 \times 10^2$ K per electron, the first term $-g_{2z^2-r^2} O_{2z^2-r^2} \epsilon_{yz}$ in Eq. (20) is important for the critical divergence of the attenuation coefficient $\alpha_{66}$ and the softening of the elastic constant $C_{6v}$ around the structural transition. The little softening of $(C_{11} - C_{12})/2$ in the present experiments implies that the second term $-g_{2y'y'} O_{2y'y'} \epsilon_{y'y'y'}$ in Eq. (20) scarcely affects the system. We schematically show the quadrupole $O_{2y'y'}$ conjugate to the strain $\epsilon_{y'y'y'}$ in Fig. 5(a) and the quadrupole $O_{2y'y'}$ conjugate with $\epsilon_{yz}$ in Fig. 5(b).

Next, we consider the interaction of the rotation $\omega_{x'y'}$ associated with the transverse ultrasonic wave with one-electron states having the angular momentum $l_z$ in the CEF Hamiltonian. The rotation operator of $\exp[-i\omega_{x'y'} \hat{z}]$ twists the $\psi_{yz}$ and $\psi_{x'y'}$ orbital states in the CEF Hamiltonian given by Eq. (10) as

\[ \langle \Gamma | H_{\text{CEF}}(\omega_{x'y'}) | \Gamma' \rangle = \int d\omega' \psi_{\omega'}(r) e^{i\omega_{x'y'} \omega_{y'y'y'} - i\omega_{x'y'} \omega_{y'y'y'}} \psi_{\omega}(r). \]

(21)

Here, $\ket{\Gamma}$ is the orbital state $l = y'$ of Eq. (12) and $\omega_{x'y'}$ of Eq. (13). Supposing infinitesimal rotation of $\omega_{x'y'} \ll 1$ associated with the ultrasound in experiments, the rotation-operated Hamiltonian of Eq. (21) is expanded in terms of power series up to the second order of $\omega_{x'y'}$ as

\[ e^{i\omega_{x'y'} \omega_{y'y'y'}} H_{\text{CEF}} e^{-i\omega_{x'y'} \omega_{y'y'y'}} = \text{H}_{\text{CEF}} + i[l_z, H_{\text{CEF}}] \omega_{x'y'} - \frac{1}{2} [l_z, l_z, H_{\text{CEF}}] (\omega_{x'y'})^2. \]

(22)

Here, $[A, B] = AB - BA$ denotes the Poisson bracket. Applying the differential operation of $l_z = -(i\partial/\partial y' + y'\partial/\partial x') = -i\partial/\partial \phi$ to the CEF Hamiltonian of Eq. (10), we obtain the perturbation Hamiltonian as

\[ H_{\text{rot}}(\omega_{x'y'}) = 4A_1^2 H_{2}^2 \omega_{x'y'} - 8A_1^2 H_{4}^2 (\omega_{x'y'})^2. \]

(23)

The first term of Eq. (23) represents the linear coupling of the rotation $\omega_{x'y'}$ to the electric hexadecapole $H_{2}^2 = \sqrt{35}(x'^2 - y'^2)/(2r^4)$ with $A_2$ symmetry of the $D_{2h}$ point group. $^{56}$ In Fig. 5(c), we schematically show the hexadecapole $H_{2}^2$ carried by the one-electron state and the rotation $\omega_{x'y'}$ in the interaction Hamiltonian $H_{\text{rot}}(\omega_{x'y'})$ of Eq. (23). The second term in Eq. (23) is the coupling of the square of the rotation $(\omega_{x'y'})^2$ to the electric hexadecapole $H_{4}^2 = \sqrt{5}(x'^4 - 6x'^2y'^2 + 2y'^4)/(8r^6)$ with

\[ \text{Fig. 5. (Color online) Schematic view of interactions between electric quadrupole } O_{2y'y'} \text{ and strain } \epsilon_{y'y'y'} \text{ with } A_1 \text{ symmetry in (a), } O_{x'y'y'} \text{ and } \epsilon_{yz} \text{ with } B_1 \text{ symmetry in (b), and electric hexadecapole } H_{4}^2 = \partial^2 H_{2}^2 \text{ and rotation } \omega_{x'y'} \text{ with } A_2 \text{ symmetry in (c) of the space group } \text{D}_{2h}^2 \text{ in the present iron precipitate. The coordinates of } x \text{ and } y \text{ (} x' \text{ and } y' \text{) are adopted for the neighboring Ba-Ba (Fe-Fe) directions.} \]
full symmetry. The hexadecapole $H_4^2$ has already appeared in the CEF Hamiltonian of Eq. (10).

The coefficient proportional to the rotation $\omega_{xy}$ in Eq. (22) is identified with the Heisenberg equation of the angular momentum $l_z$ for the CEF Hamiltonian of Eq. (10). This gives the time derivative of the angular momentum $l_z$, which is identical to the torque $\tau_{xy}$ for a quantum system, as

$$\hbar \frac{\partial l_z}{\partial t} = [l_z, H_{\text{CEF}}] = -i g H_4 = i \tau_{xy}. \quad (24)$$

Note that the coupling parameter of $g_H = 4A_4^z$ in Eq. (24) has already been given in the CEF Hamiltonian of Eq. (10). Since the angular momentum $l_z$ is constant for the motion of the one-electron states in the CEF Hamiltonian of Eq. (10), $l_z$ commutes with $H_{\text{CEF}}$ as $[l_z, H_{\text{CEF}}] = 0$. Consequently, the hexadecapole $H_4^2$ proportional to the time derivative of the angular momentum $\partial l_z/\partial t$ of Eq. (24) is expected to vanish. This is well known as the rotational invariance for the electronic states in a central force potential such as the CEF potential. The rotation invariance can be naturally understood by the fact that the hexadecapole interaction of Eq. (22) does not change the energy of an electron moving along the contour line of the CEF potential.

The rotation $\omega_{xy}$ due to a transverse ultrasonic wave should also affect the quadrupole-strain interaction of Eq. (20) within the bilinear coupling between the strain and rotation as

$$H_{\text{QS}}^\text{xy} (\omega_{xy}) = \sum_{i,j} \langle \omega_{xy} \rangle \left[ O_{\text{xy}} \right]_{ij} \chi_{ij} \omega_{xy}$$

$$= 2 g_{xy} \left[ O_{\text{xy}} \right] \chi_{xy} \omega_{xy} \quad (25)$$

Here, the commutation relation among the Pauli matrices of Eq. (18) is employed. The perturbation energies for the one-electron states $l = y^z$ and $z^x$ with energy $E_{l}^0$ due to the perturbation Hamiltonian of Eq. (25) are written as

$$E_l (\omega_{xy}) = E_{l}^0 + \langle l | H_{\text{QS}}^\text{xy} (\omega_{xy}) | l \rangle$$

$$= E_{l}^0 + 2 g_{xy} \langle l | O_{\text{xy}} | l \rangle \chi_{xy} \omega_{xy}$$

$$- 2 g_{zy} \langle l | O_{\text{zy}} | l \rangle \chi_{zy} \omega_{xy} \quad (26)$$

The null of the diagonal elements of the Pauli matrix of $O_{\text{xy}}$ of Eq. (15) diminishes the second term $2 g_{xy} \langle l | O_{\text{xy}} | l \rangle \chi_{xy}$ in the second line in Eq. (26). Although the matrix of $O_{\text{zy}}$ of Eq. (17) possesses diagonal elements, we may ignore the third term $-2 g_{zy} \langle l | O_{\text{zy}} | l \rangle \chi_{zy}$ in the second line in Eq. (26) because the little softening of $(C_{11} - C_{12})/2 \leq 1$. Presumably, the strain-rotation bilinear coupling terms of Eq. (25) have little effect on the present system with degenerate $y^z$ and $z^x$ orbitals.

The applied magnetic field, however, breaks the rotational invariance for the one-electron states in the CEF potential. This effect of rotation on the elastic properties in applied magnetic fields has been theoretically investigated and experimentally verified by ultrasonic measurements on the antiferromagnetic compound MnF$_2$ and the rare-earth compounds TbSm, CeAl$_3$, CeBe, CeLa, CeAl$_5$, and HoVO$_4$. Furthermore, the effect of rotation on the quantum oscillation of elastic constants of transverse ultrasonic waves for Fermi surfaces with an ellipsoidal shape has been discussed. In Sect. 4.6, we show the coupling of the rotation associated with the transverse acoustic phonons to the hexadecapole carried by two-electron states.

### 4.3 Quadrupole-strain interaction

As shown in Eq. (20), the quadrupoles carried by electrons in the CEF Hamiltonian interact to the strains of transverse ultrasonic waves. This quadrupole-strain interaction brings about the sizable softening of $C_{66}$ and the divergence of the attenuation coefficients $\alpha_6$ and $\alpha_{1110}$ around the structural transition. In order to properly describe the structural transition of the iron pnictide, we will consider the interaction of the quadrupole $O_{\text{xy}} (r_i)$ with the transverse acoustic phonons carrying the strain $\epsilon_{xy} (r_i)$ for the position vector $r_i$ as electron as

$$H_{\text{QS}} = -g_{xy} \sum_{h,l,m,n} \sum_{\sigma=\uparrow,\downarrow} \int d^3r \left[ \epsilon_{xy} (r_i) \right] \Psi_{h,l,m,n} (r_i) \Psi_{h,l,m,n}^\dagger (r_i) \quad (27)$$

The electron field operators of $\Psi_{h,l,m,n} (r_i) \Psi_{h,l,m,n}^\dagger (r_i)$ at position $r_i$ acting on the degenerate $y^z$ and $z^x$ bands with spin orientation $\sigma$ in Eq. (27) are written as

$$\Psi_{h,l,m,n} (r_i) = d_{h,l,m,n} \psi_{h,l,m,n}^\dagger (r_i) \quad (28)$$

$$\Psi_{h,l,m,n}^\dagger (r_i) = d_{h,l,m,n}^\dagger \psi_{h,l,m,n} (r_i) \quad (29)$$

Here, $l$ denotes the band suffix of $y^z$ and $z^x$, and $\psi_{h,l,m,n} (r_i)$ is the spin function of $\sigma (r_i)$ for up-spin $\sigma = \uparrow$ or down-spin $\sigma = \downarrow$. The annihilation operator $d_{h,l,m,n}$ and creation operator $d_{h,l,m,n}^\dagger$ are expressed by Fourier transforms as below

$$d_{h,l,m,n} = \sum_k d_{h,l,m,n} e^{i k r_i} \quad (30)$$

$$d_{h,l,m,n}^\dagger = \sum_k d_{h,l,m,n}^\dagger e^{-i k r_i} \quad (31)$$

Here, $k$ is the wavevector of an electron. We express the Hamiltonian $H_K$ for the electrons accommodated in the degenerate $y^z$ and $z^x$ bands, which play a significant role in the appearance of the quadrupole ordering in the system as

$$H_K = \sum_k \sum_{\sigma} \left[ E_{\text{xy}^z} (k) d_{h,l,m,n}^\dagger \chi_{xy} \epsilon_{xy} \right]$$

$$+ \sum_{k} \left[ E_{\text{zy}}^x (k) d_{h,l,m,n}^\dagger \chi_{zy} \epsilon_{zy} \right] \quad (32)$$

Here, $\epsilon_{xy} (k)$ for suffix $l = y^z$ or $z^x$ is the energy from the Fermi level.

The quadrupole-strain interaction of Eq. (27) is rewritten in terms of Fourier transforms as

$$H_{\text{QS}} = -G_{\text{xy}^z} \sum_{k,q} O_{\text{xy}^z} (k,q,\epsilon_{xy}) \quad (33)$$

Here, we use the coupling constant $G_{\text{xy}^z} = \sqrt{3} g_{xy} / 7$. The interaction Hamiltonian of Eq. (33) means that the electrons with wavevector $k$ bearing the quadrupole $O_{\text{xy}^z} (k,q)$ are scattered by the strain $\epsilon_{xy} (q)$ of the transverse acoustic phonons with wavevector $q$. The quadrupole $O_{\text{xy}^z} (k,q)$ in Eq. (33) is described in terms of the annihilation and creation operators of Eqs. (30) and (31) as

$$O_{\text{xy}^z} (k,q) = \sum_{\sigma} \left[ -d_{h,l,m,n}^\dagger \chi_{xy} \epsilon_{xy} \right]$$

$$+ \sum_{k} \left[ d_{h,l,m,n}^\dagger \chi_{zy} \epsilon_{zy} \right] \quad (34)$$
Note that the quadrupole $O_{z^2-y^2}, k, q$ in Eq. (34) is simply described by the difference between the occupation numbers for the degenerate $y'z$ and $z'x$ bands at the long-wavelength limit of $|q| = 2\pi/\lambda \to 0$ of the transverse acoustic phonons carrying the strain $e_{xy}(q)$ as

$$
O_{z^2-y^2}, k, q = \sum_{\sigma} \left( -d^\dagger_{k', y', \sigma, \sigma'} d_{k, y, \sigma} + d^\dagger_{k, z, \sigma} d_{k', z', \sigma} \right)
$$

$$
= \sum_{\sigma} \left( -n_{k', y', \sigma} + n_{k, z, \sigma} \right).
$$

In Sect. 4.6, we will use the quadrupole $O_{z^2-y^2}, k, q$ expressed as

$$
O_{z^2-y^2}, k, q = \sum_{\sigma} \left( d^\dagger_{k, q, y', \sigma} d_{k, z, \sigma} + d^\dagger_{k, q, z', \sigma} d_{k', y, \sigma} \right).
$$

The strain $e_{xy}(q)$ in Eq. (33) is expressed by the annihilation and creation operators of phonons defined in Eq. (8) as

$$
e_{xy}(q) = i \frac{\hbar}{2V_{PM\omega_{y}}} q^x \left( a_{x, q} - a_{x, -q}^\dagger \right)
$$

$$
+ i \frac{\hbar}{2V_{PM\omega_{y}}} q^y \left( a_{y, q} - a_{y, -q}^\dagger \right).
$$

The strain $e_{xy}$ induced by a transverse ultrasonic wave with frequency as low as 100 MHz is identified with $e_{xy}(q)$ of Eq. (37) in the long-wavelength limit of $|q| = 2\pi/\lambda \to 0$ as $e_{xy} = e_{xy}(q = 0)$. In the case of the quadrupole-strain interaction of Eq. (33) mediated by thermally excited transverse acoustic phonons, the emission of phonons carrying the strain $e_{xy}(q)$ scatters the electron state of momentum $\hbar k$ to the state of $\hbar k + \hbar q$ and the absorption of phonons scatters the electron state of $\hbar k$ to the state of $\hbar k - \hbar q$.

The canonical transformation for the electron-phonon scattering processes by the quadrupole-strain interaction $H_{Q\text{S}}$ of Eq. (33) provides us with the electron interaction mediated by the transverse acoustic phonons as

$$
H_{Q\text{S}}^{\text{ind}} = - \sum_{k, k', q, \sigma, \sigma'} D_{Q\text{S}}^{\text{QQ}}(k, q) d^\dagger_{k, q, y', \sigma} d_{k, z, \sigma} d^\dagger_{k, q, z', \sigma} d_{k', y, \sigma} + \text{H.c.}
$$

$$
+ \sum_{k, k', q, \sigma, \sigma'} D_{Q\text{S}}^{\text{QQ}}(k, q) d^\dagger_{k, q, y', \sigma} d_{k, z, \sigma} d^\dagger_{k, q, z', \sigma} d_{k', y, \sigma} + \text{H.c.}
$$

$$
+ \sum_{k, k', q, \sigma, \sigma'} D_{Q\text{S}}^{\text{QQ}}(k, q) d^\dagger_{k, q, z', \sigma} d_{k, z, \sigma} d^\dagger_{k, q, y', \sigma} d_{k', y, \sigma} + \text{H.c.}
$$

$$
- \sum_{k, k', q, \sigma, \sigma'} D_{Q\text{S}}^{\text{QQ}}(k, q) d^\dagger_{k, q, y', \sigma} d_{k, z, \sigma} d^\dagger_{k, q, z', \sigma} d_{k', y, \sigma} + \text{H.c.}
$$

Here, the coupling coefficient $D_{Q\text{S}}^{\text{QQ}}(k, q)$ in Eq. (38) for $l = y'$ and $z'$ is given by

$$
D_{Q\text{S}}^{\text{QQ}}(k, q) = \frac{1}{2} G_{x^2-y^2}^2
$$

$$
\times \left\{ \frac{\hbar}{2V_{PM\omega_{y}}} q^2 \left[ \omega_{y}(q) - \omega_{y}(k - q) \right]^2 - \hbar \omega_{y}(q)^2 \right\}
$$

$$
+ \frac{\hbar}{2V_{PM\omega_{y}}} q^2 \left[ \omega_{y}(q) - \omega_{y}(k - q) \right]^2 - \hbar \omega_{y}(q)^2 \right\}
$$

The four independent scattering processes involving virtually excited one-phonon states due to the strain $e_{xy}(q)$ in Eq. (33) are schematically pictured in Fig. 6. The processes in Fig. 6(a) indicate the scattering of the electrons accommodated in the same band $y'z$ and those in Fig. 6(d) indicate the scattering in the same band $z'x$. The processes in Figs. 6(b) and 6(c) indicate the scattering between two electrons in the different bands $y'z$ and $z'x$.

Supposing the identity of the energy $e_{y'z}(k) = e_{z'x}(k)$ for electrons with a small wavevector $k$ located near the Fermi level, we take the indirect quadrupole interaction coefficient $D_{Q\text{S}}^{\text{QQ}}(k, q) = D_{Q\text{S}}^{\text{QQ}}(k, q) = D_{Q\text{S}}^{\text{QQ}}(k, q)$ in the tetragonal phase. Using the quadrupole interaction $O_{z^2-y^2}, k, q$ expressed in Eq. (34), we reduce the quadrupole interaction Hamiltonian of Eq. (38) as

$$
H_{Q\text{S}}^{\text{ind}} = - \sum_{k, k', q} D_{Q\text{S}}^{\text{QQ}}(k, q) O_{z^2-y^2}, k, q O_{z^2-y^2}, k', q.
$$

In order to understand the frequency dependence of the ultrasonic attenuation of $\alpha_{l[110]}$ in Fig. 3(a), we will examine the indirect quadrupole interaction coefficient $D_{Q\text{S}}^{\text{QQ}}(k, q)$ in Eq. (40), which strongly depends on the magnitude of wavevectors $k$ and $k'$ for the interacting electrons and $q$ for the transverse acoustic phonons participating in the scattering. Taking the electron energies of $e_{y'z}(k) = e_{z'x}(k) = \epsilon(k) = h^2|k|^2/2m_e$ with effective electron mass $m_e$ and transverse acoustic phonon energies of $\omega_{y}(q) = \omega_{z}(q) = \omega_{z}(q)$ with ultrasonic velocity $v_{us}$, we obtain the indirect quadrupole interaction coefficient $D_{Q\text{S}}^{\text{QQ}}(k, q)$ of Eq. (40) as

$$
D_{Q\text{S}}^{\text{QQ}}(k, q) = -G_{x^2-y^2}^2 \frac{\hbar}{2V_{PM\omega_{y}}} q^2
$$

$$
\times \frac{\hbar \omega_{y}(q)}{[\epsilon(k) - \epsilon(k - q)]^2 - \hbar^2 \omega_{y}(q)^2}.
$$

In the small-wavenumber limit of $|q| \to 0$ for the transverse acoustic phonons, the indirect quadrupole interaction coefficient of Eq. (41) is reduced to the simple formula

$$
D_{Q\text{S}}^{\text{QQ}}(k, q = 0) = -G_{x^2-y^2}^2 \frac{\hbar}{2V_{PM}} \left( \frac{\hbar}{m_e} \right)^2 \frac{1}{[k^2 - m_e^2 v_{us}^2]}. \quad (42)
$$
The indirect quadrupole interaction coefficient of Eq. (42) for electrons with a small wavenumber of \(-k_b^Q < k < k_b^Q\) = \(m_e v_{6b}/h\) has a positive sign, \(D_{QQ}(k, q = 0) > 0\), showing the ferro-type quadrupole interaction, while the interaction coefficient for a relatively large wavenumber \(k > k_b^Q\) = \(m_e v_{6b}/h\) possesses a negative sign, \(D_{QQ}(k, q = 0) < 0\), indicating the antiferro-type quadrupole interaction. The ferro-type interaction of \(D_{QQ}(k, q = 0) > 0\) brings about the ferro-quadrupole ordering accompanying the structural transition, as actually observed in the under-doped compound \(x = 0.036\).

It is worth estimating the boundary wavenumber \(k_b^Q = |k_b^Q|\) and the corresponding energy for the present iron pnictide. In the compound with \(x = 0.036\), the ultrasonic velocity \(v_{6b} = 772\) m/s at 65 K in the vicinity of the structural transition \((1780\) m/s at 100 K far above the transition) gives the boundary wavenumber \(k_b^Q = 6.7 \times 10^6\) m\(^{-1}\) \((15 \times 10^6\) m\(^{-1}\), the boundary wavelength \(\lambda_b^Q = 0.94 \times 10^{-6}\) m, and the corresponding frequency \(f_b^Q = \varepsilon(k_b^Q)/h = 0.41\) GHz \((2.2\) GHz). Here, we take the electron rest mass as \(m_e\).

In the low-energy regime below 2 GHz \(\approx 100\) mK, therefore, the electrons bearing the quadrupoles \(O_{c\sigma'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) and \(O_{c\pi'\gamma':\kappa'\lambda'\eta'\lambda''}\) in Eq. (40) interact with each other through the strain \(\varepsilon_{\kappa\eta}(q)\) in the manner of the ferro-type quadrupole interaction. Actually, the relaxation rate \(\tau^{-1}\) observed around the structural transition for \(x = 0.036\) in Fig. 3(b) is always smaller than the estimated crossover frequency of about 2 GHz. This implies that the transverse acoustic waves with frequencies below 2 GHz exhibit the full extent of elastic softening and considerable damping in the vicinity of the structural transition point, while the acoustic waves with frequencies higher than 2 GHz exhibit less softening and damping. As shown in Fig. 2(e), the ultrasonic measurements with frequencies less than 260 MHz actually exhibited the full amount of softening in \(C_{6b}\), while the Raman scattering measurements of the transverse acoustic phonons with frequencies as high as 20 GHz in the end material \(x = 0\) exhibited only 25% of the full amount of softening.\(^{64}\)

### 4.4 Quadrupole interaction

The electrons accommodated in the degenerate \(y'z'\) and \(zx'\) bands carry the quadrupoles. In addition to the indirect quadrupole interaction \(H_{\text{ind}}^Q\) mediated by the strain \(\varepsilon_{\kappa\eta}\) presented in Sect. 4.3, we expect direct quadrupole interactions through the long-range Coulomb potential between electrons at positions \(r_i\) and \(r_j\), expressed as

\[
\langle l_1 \sigma, l_2 \sigma' | H_{\text{Coulomb}} | l_3 \sigma', l_4 \sigma \rangle = \sum_{i < j} \int \int dr_i dr_j \psi_{l_1}^*(r_i) \psi_{l_2}^*(r_j) \psi_{l_3}^*(r_i) \psi_{l_4}^*(r_j) \times \frac{e^2}{|r_i - r_j|} \psi_{l_1}(r_i) \psi_{l_2}(r_j) \psi_{l_3}(r_i) \psi_{l_4}(r_j).
\]

Here, \(l_n (n = 1, 2, 3, 4)\) denote suffixes of \(y'z'\) and \(zx'\) orbital bands and \(\psi_{l_n}\) is the spin function in Eqs. (28) and (29). The electric multipole expansion for the Coulomb interaction in Eq. (43) for an isotropic space with \(r_i < r_j\) provides terms consisting of the monopole, dipole, and quadrupole as\(^{56, 65}\)

\[
\frac{e^2}{|r_i - r_j|} = \frac{e^2}{r_j} \sum_{k=0}^{\infty} \frac{4\pi}{2k + 1} \left( \frac{r_j}{r_i} \right)^k \sum_{\mu = -k}^{k} Y_k^\mu(\theta_j, \varphi_j) Y_k^\mu(\theta_i, \varphi_i).
\]

According to the multipole expansion of Eq. (44), we identify the electric quadrupole with the order parameter of the structural transition in the present iron pnictide. In our attempt to clarify the spontaneous symmetry breaking of the degenerate \(y'z'\) and \(zx'\) orbital bands in the tetragonal lattice, we express the direct quadrupole interaction \(H_{\text{ind}}^Q\) in terms of the quadrupole \(O_{c\sigma'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) with the \(B_2\) symmetry and \(O_{c\pi'\gamma':\kappa'\lambda'\eta'\lambda''}\) with \(B_1\) symmetry as

\[
H_{\text{ind}}^{QQ} = - \sum_{i < j} J_{ij}(r_i - r_j) \times [O_{c\sigma'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}(r_i) + O_{c\pi'\gamma':\kappa'\lambda'\eta'\lambda''}(r_i)].
\]

Here, we adopt the Coulomb interaction coefficient \(J_{ij}(r_i - r_j)\), which depends on the relative position \(r_i - r_j\). The quadrupole interaction of \(O_{c\sigma'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) with \(A_1\) symmetry is excluded because symmetry breaking is not expected. The case of quadrupoles \(O_{c\pi'\gamma':\kappa'\lambda'\eta'\lambda''}\) being absent in the \(y'z'\) and \(zx'\) bands is beyond the scope of this study. Note that the monopole interaction among the electrons in Eq. (44) is effectively included in the band model concerned and that the dipole interaction is irrelevant for the present lattice bearing the inversion symmetry in the \(xy\) plane.

Using the expressions \(O_{c\pi'\gamma':\kappa'\lambda'\eta'\lambda''} = \sqrt{3} r_{\pi'\gamma'}/7\) in Eq. (15) and \(O_{c\sigma'\gamma':\pi'\kappa'\lambda'\eta'\lambda''} = \sqrt{3} r_{\sigma'\gamma'}/7\) in Eq. (17), we map the quadrupole interaction of Eq. (45) on the ideal \(xz\) model. In the present real system, however, the deviation of the anisotropic quadrupole interaction from the ideal \(xz\) model is expected. From the viewpoint of the symmetry of the tetragonal lattice, the mutual quadrupole interactions of \(O_{c\pi'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) with \(B_2\) symmetry and \(O_{c\pi'\gamma':\kappa'\lambda'\eta'\lambda''}\) with \(B_1\) symmetry may be different. Actually, it has been reported that the mixing between the \(4p\) states of As ions and the \(3d\) states of Fe ions brings about an anisotropic quadrupole interaction.\(^{64}\) The quadrupoles \(O_{c\pi'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) at positions \(r_i\) and \(r_j\) interact with each other through the strain \(\varepsilon_{\kappa\eta}\) of the transverse acoustic phonons for \(C_{6b}\), which exhibits the large amount of softening. The quadrupoles \(O_{c\pi'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) also interact with each other mediated by the strain \(\varepsilon_{\kappa\eta}\) of the transverse acoustic phonons for \((C_{11} - C_{12})/2\), which monotonically increases. The former quadrupole interaction of \(O_{c\pi'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) plays a significant role in the structural transition, while the latter quadrupole interaction of \(O_{c\pi'\gamma':\pi'\kappa'\lambda'\eta'\lambda''}\) has a minor effect on the phase transition. Consequently, the indirect quadrupole interaction mediated by the transverse acoustic phonons also indicates the anisotropic nature of the quadrupole interaction.

Combining the direct quadrupole interaction \(H_{\text{ind}}^{QQ}\) of Eq. (44) followed by the Coulomb potential and the indirect interaction, we obtain the total quadrupole interaction as...
quadrupole interaction $H_{\text{QQ}}^{Q0}$ of Eq. (40) mediated by the strain $\varepsilon_{xy}$ of the transverse acoustic phonons, we obtain the anisotropic quadrupole interaction $H_{\text{QQ}}$ specified by parameter $\gamma$ as

$$H_{\text{QQ}}(\gamma) = -\sum_{k \neq j} J_{\text{Q}}(r_i - r_j) \times \left[ O_{x_i} O_{x_j} + \gamma O_{x_i} O_{y_j} + \gamma O_{y_i} O_{y_j} \right].$$

(46)

The quadrupole interaction coefficient $J_{\text{Q}}(r_i - r_j)$ in Eq. (46) is written as the sum of the Coulomb interaction coefficient $J_c(\gamma)$ in the direct interaction of Eq. (45) and the indirect quadrupole interaction coefficient $D^{QQ}(r_i - r_j)$ mediated by the strain $\varepsilon_{xy}$ of the transverse acoustic phonons in Eq. (41).

$$J_{\text{Q}}(r_i - r_j) = J_c(r_i - r_j) + D^{QQ}(r_i - r_j).$$

(47)

The quadrupole interaction coefficient $J_c(r_i - r_j)$ and the anisotropic parameter $\gamma$ in Eq. (46) play a substantial role in the appearance of the ferro-quadrupole ordering associated with the superconducting transition.

### 4.5 Quadrupole ordering

In order to explain the elastic softening of $C_{66}$ and critical slowing down of the relaxation time $\tau$ around the structural transition in the iron pnictide, we consider the quadrupole interaction Hamiltonian $H_{\text{QQ}}(\gamma)$ of Eq. (46) for the case of $\gamma = 0$ mapped on the Ising model. A transverse ultrasonic wave with a small-wavenumber limit of $|q| \rightarrow 0$ induces the strain $\varepsilon_{xy} = \varepsilon_{xy} (q = 0)$, which is treated as a classical quantity. According to the quadrupole-strain interaction of Eq. (33), the strain $\varepsilon_{xy}$ generated by the ultrasonic wave lifts the degenerate $y'$ and $z'$ bands, as schematically shown in Fig. 7(a).

This ultrasonic perturbation gives a quadrupole susceptibility proportional to the reciprocal temperature as

$$\chi_Q = \frac{N_0 G_{2x-2y}^0 / C_{66}^0}{T} = \frac{\Delta Q}{T}.$$  

(48)

Here, $N_0$ is the number of electrons carrying the ferro-type quadrupole interaction in the small-wavenumber regime of $-k_b^0 < k < k_b^0$ for the boundary wavenumber $k_b^0$ as discussed for Eq. (42). The quadrupole-strain interaction energy of $\Delta Q = N_0 G_{2x-2y}^0 / C_{66}^0$ in Eq. (48) is determined in terms of $D^{QQ}(k, q)$ of Eq. (42) for the small-wavenumber regime of $|q| \rightarrow 0$ as

$$\Delta Q = \frac{C_{66}^0}{2VN_0 \rho_m V_{\text{m66}}} = \frac{G_{2x-2y}^0}{2V \rho_m V_{\text{m66}}} = \frac{1}{N_0} \sum_{|k| < k_b^0} D^{QQ}(k, q = 0) = \bar{D}^{QQ}.$$  

(49)

Here, $\Sigma_{|k| < k_b^0}$ means the sum over the electron states with wavenumber $|k| < k_b^0$ that participate in the ferro-type quadrupole interaction. $\bar{D}^{QQ}$ in Eq. (49) stands for the effective indirect quadrupole interaction of Eq. (41). As shown in Fig. 4, the ultrasonic experiments give a quadrupole-strain interaction energy of $\Delta Q \approx 20$ K that is almost independent of the Co concentration $x$. The indirect quadrupole interaction energy $D^{QQ}$ in Eq. (49) is enhanced by the softening of $\rho_m V_{\text{m66}}^2 = C_{66}$ due to the quadrupole-strain interaction of Eq. (33).

The softening of $C_{66}$ as a precursor of the structural transition is expressed as

$$C_{66} = C_{66}^0 (1 - \chi_Q) = C_{66}^0 \left( 1 - \frac{T - T_0}{\Theta_Q} \right) = C_{66}^0 \left( 1 - \frac{\Delta Q}{T - \Theta_Q} \right).$$  

(50)

Here, we adopt the renormalized susceptibility $\chi_Q$ expressed by the quadrupole interaction energy $\Theta_Q$ and the quadrupole-strain interaction energy $\Delta Q$ as

$$\chi_Q = \frac{\Delta Q}{T - \Theta_Q}.$$  

(51)

The elastic instability point due to the full softening $C_{66} \rightarrow 0$ gives the structural transition temperature as $T_0 = \Theta_Q + \Delta Q$. This has already been used in Eq. (2) for the analysis of the experimentally observed softening of $C_{66}$.

By using the mean field approximation, we obtain the following self-consistent equation giving the temperature dependence of the quadrupole order parameter $O_{x^2-y^2}$:

$$\left\langle O_{x^2-y^2} \right\rangle = \tanh \left[ \tilde{J}_Q \left\langle O_{x^2-y^2} \right\rangle / k_B T \right].$$  

(52)

Here, $\langle A \rangle$ stands for the thermal average. We use the effective coupling constant $\tilde{J}_Q$, which is the average of the Fourier transformed quadrupole interaction of $J_Q(r_i - r_j)$ as

$$\tilde{J}_Q = \frac{1}{N_0} \sum_{|k| < k_b^0} J_Q(k, q = 0).$$  

(53)

Finally, the effective coupling constant $\tilde{J}_Q$ is determined by the physical properties of the compounds.
ferro-quadrupole ordering as group \(\langle\) below the ferro-quadrupole ordering point of \(T\) to be a non vanishing solution of \(\tilde{\epsilon}_Q\). Here, \(\tilde{\epsilon}_Q\) is the effective energy of the direct Coulomb interaction of Eq. (45). \(\tilde{D}^{QQ}\) is the effective indirect quadrupole interaction coefficient in Eq. (49). We suppose that the ferro-quadrupole ordering is caused by the quadrupole interaction with the positive coupling constant \(\tilde{J}_Q > 0\). We expect there to be a non vanishing solution \(\langle O_{\tilde{Q}_{x'y'z'}} \rangle \neq 0\) at low temperatures below the ferro-quadrupole ordering point of \(T_c = \tilde{J}_Q/k_B\).

The elastic instability due to the full softening \(C_{66} \to 0\) brings about spontaneous lattice distortion accompanying the ferro-quadrupole ordering as

\[
\langle \epsilon_N \rangle = N_Q G_{\tilde{Q}_{x'y'z'}} \frac{\langle O_{\tilde{Q}_{x'y'z'}} \rangle}{C_{66}} = \sqrt{N_Q D_Q A_O} \langle O_{\tilde{Q}_{x'y'z'}} \rangle. \tag{54}
\]

Here, we use the relation between the coupling constant \(G_{\tilde{Q}_{x'y'z'}}\) and the quadrupole-strain interaction energy \(D_Q\) of \(G_{\tilde{Q}_{x'y'z'}} = \sqrt{D_Q N_Q/6}\). The ferro-quadrupole ordering of \(\langle O_{\tilde{Q}_{x'y'z'}} \rangle \neq 0\) associated with the spontaneous strain of \(\langle \epsilon_N \rangle \neq 0\) in Eq. (54) is caused by the structural transition from the tetragonal phase with the high-symmetry space group \(D_{4h}^{17}\) to the orthorhombic phase with the low-symmetry space group \(D_{2h}^{15}\). The generators of the symmorphic space group \(D_{4h}^{17}\) consist of the rotation, reflection, and inversion operations but do not involve the screw and glide operations. The quenching of the \(B_{2g}\) symmetry in the mother phase of \(D_{2h}^{15}\) associated with the ferro-quadrupole ordering of \(\langle O_{\tilde{Q}_{x'y'z'}} \rangle \neq 0\) and the spontaneous strain \(\langle \epsilon_N \rangle \neq 0\) across the structural transition loses the symmetry operations, which consist of rotation through \(\pm \pi/2\) about the vertical axis of \(C_4\), rotations through \(\pi\) about the horizontal \(x\)- and \(y\)-axes of \(2C_2\), rotation through \(\pm \pi/2\) about the vertical axis followed by inversion of \(2\Gamma C_4\), and mirror reflection in the vertical plane of \(2\Gamma C_4\). Note that the ferro-type quadrupole ordering denoted in the present paper has been frequently referred to as cooperative Jahn-Teller effects, orbital orderings, or electronic nematic orders.

The neutron scattering experiments on the end material BaFe₂As₂ have shown a spontaneous strain \(\langle \epsilon_N \rangle\) of \(5.08 \times 10^{-3}\) at \(5\) in the distorted orthorhombic phase, where the order parameter is fully polarized as \(\langle O_{\tilde{Q}_{x'y'z'}} \rangle = 1\). Adopting the quadrupole-strain interaction energy \(D_Q = 21\) K and the elastic constant \(C_{66} = 3.19 \times 10^{10}\) J/m³ of BaFe₂As₂, we estimate the number of 3d electrons \(N_Q\) in Eq. (54) to be \(2.84 \times 10^{13}\) cm⁻³, which is approximately one-fourteenth of the total number of electrons of \(2N_{Fe} = 3.92 \times 10^{13}\) cm⁻³. Furthermore, we deduce the coupling energy \(G_{\tilde{Q}_{x'y'z'}}\) to be \(\sim 4 \times 10^3\) K per electron, which is four times larger than the tentatively estimated \(G_{\tilde{Q}_{x'y'z'}}\) of \(\sim 1 \times 10^3\) K for the localized electron picture in Sect. 3.1. The large quadrupole-strain coupling energy of \(G_{\tilde{Q}_{x'y'z'}} \sim 4 \times 10^3\) K is caused by the enhanced quadrupole due to the extended orbital radius compatible with the itinerant feature of the 3d electron bands. Taking the number of 3d electrons \(N_Q = 2.84 \times 10^{21}\) cm⁻³ into account, we may roughly estimate the indirect quadrupole interaction energy in BaFe₂As₂ as \(D^{QQ} \sim 220\) K at \(T = T_c = 135\) K for \(d_0 = 21\) K, \(C_{66} = 3.19 \times 10^{10}\) J/m³, and \(C_{66} = \rho N_{Fe}^2 = 0.281 \times 10^{10}\) J/m³. This value is comparable with the structural transition temperature \(T_s\) of the under-doped compounds. It is worth referring to the extremely enhanced quadrupole-strain interaction energy of \(2.8 \times 10^3\) K for the vacancy orbital of a silicon wafer with a large orbital radius, which was verified by means of bulk ultrasonic waves and surface acoustic waves.

The divergence of the relaxation time \(\tau\) observed via the ultrasonic attenuation coefficient \(a_{66}\) for \(x = 0.036\) in Fig. 3(b) is expressed in terms of the critical slowing down due to freezing of the ferro-quadrupole order parameter \(O_{\tilde{Q}_{x'y'z'}}\) at the structural transition temperature \(T^*_c \approx T^*_o = 65\) K. The relaxation time \(\tau_Q\) is written as

\[
\tau_Q = \tau_0 \left| \frac{T - T^*_c}{T^*_o} \right|^{-1} \propto \frac{1}{1 - \chi_Q}. \tag{55}
\]

This expression for \(\tau_Q\) based on the degenerate \(y'z'\) and \(z'x'\) bands well reproduces the experimental results analyzed in terms of Eq. (4) for the critical index \(2\nu = 1\) for both tetragonal and orthorhombic phases. The critical slowing down of the quadrupole \(O_{\tilde{Q}_{x'y'z'}}\) in the present iron pnictide agrees with the critical dynamics of the kinetic Ising model. According to the dissipation fluctuation theorem, the critical slowing down of the relaxation time \(\tau_Q\) is expressed by the divergence of the susceptibility for the order parameter of the quadrupole \(O_{\tilde{Q}_{x'y'z'}}\) due to the infinite increase in the correlation length \(\xi\) in the vicinity of the structural transition. By analogy with the ferro-magnetic spin system, the development of the correlation function of \(\langle O_{\tilde{Q}_{x'y'z'}}(k,\tau)O_{\tilde{Q}_{x'y'z'}}(-k,0)\rangle\) obeying the time decay factor of \([\exp(-t/\tau_Q(k))]\) should cause the relaxation time \(\tau_Q(k)\) to diverge at the ferro-type ordering point. Knowledge of the diffusion coefficient is necessary for the numerical estimation of \(\tau_Q\) in Eq. (55).

4.6 Hexadecapole-rotation interaction of two-electron states

In the over-doped compound \(x = 0.071\) exhibiting superconductivity, the antiferro-type quadrupole interaction with the negative quadrupole interaction energy \(\Theta_Q = -47\) K is verified by analysis of the softening of \(C_{66}\) in the normal phase. The softening of \(C_{66}\) tends to zero at the fictitious structural instability point at the negative temperature \(T^*_o = -26.5\) K. This means that the critical slowing down of the relaxation time \(\tau\) around the superconducting transition at \(T^*_c = T^*_c = 23\) K in Fig. 1(b) is caused by an appropriate order parameter, which is strictly distinguished from the quadrupole. In the present section, we introduce two-electron states bound by the quadrupole interaction and consider the coupling of the hexadecapole carried by two-electron states to the rotation \(\omega_Q\) of transverse ultrasonic waves.

Taking the Pauli exclusion principle into account, we express the energy of the anisotropic quadrupole interaction of Eq. (46) by using the two-electron state \(\psi_{\Gamma, \Gamma}^{2,2}(r, r')\) of the Slater determinant with the irreducible representation \(\Gamma_s\) of the orbital part, and the spin state denoted by the total spin \(S\).
and \(z\) component \(S_z\) as

\[
E_{\Gamma}^{\Gamma_S S_z} = \{\Gamma, S S_z \}; H_{0Q}(\gamma) \Gamma, S S_z ; \]

\[
= \int dr^2 dr^2 \psi^{\Gamma_S S_z}(r, r) H_{0Q}(\gamma) \psi^{\Gamma_S S_z}(r, r). \quad (56)
\]

From the viewpoint of symmetry for the orbital state, the direct product of the \(E\)-doublet in the point group symmetry \(D_{2d}\) reduces as \(E \equiv A_1 \oplus A_2 \oplus B_1 \oplus B_2\). Thus, the symmetric \(A_1\), \(B_1\), and \(B_2\) orbital states exist upon exchanging \(r_1\) for \(r_2\), as well as the antisymmetric \(A_2\) state. Furthermore, there are two kinds of spin states consisting of a spin singlet of total spin \(S = 0\) that is symmetric upon exchanging \(r_1\) for \(r_2\) and the antisymmetric spin triplet with \(S = 1\). Consequently, we deduce the two-electron state of \(\psi^{\Gamma_S S_z}_1(r, r)\) in Eq. (56), which is denoted by the orbital state of the symmetry \(\Gamma = A_1\), \(B_2\), and \(B_1\) with the spin singlet of \(S = 0\) and the orbital state of the \(A_2\) symmetry with the spin triplet of \(S = 1\) for \(S_z = 1, 0\), and \(-1\). As a result, we obtain the Slater determinant in terms of the one-electron orbital states of \(\psi_{\gamma z}(r)\) and \(\psi_{\xi \gamma}(r)\) and the spin states of \(\alpha(r)\) and \(\beta(r)\) as

\[
\begin{align*}
\psi^{000}_{\Gamma_1 = A_1}(r, r) &= \frac{1}{\sqrt{2}} \left[ \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) + \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) \right] \\
&\times \frac{1}{\sqrt{2}} \left[ (\alpha(r) \beta(r) - \beta(r) \alpha(r)) \right], \quad (57) \\
\psi^{000}_{\Gamma_2 = B_2}(r, r) &= \frac{1}{\sqrt{2}} \left[ \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) - \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) \right] \\
&\times \frac{1}{\sqrt{2}} \left[ (\alpha(r) \beta(r) - \beta(r) \alpha(r)) \right], \quad (58) \\
\psi^{000}_{\Gamma_3 = B_1}(r, r) &= \frac{1}{\sqrt{2}} \left[ \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) + \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) \right] \\
&\times \frac{1}{\sqrt{2}} \left[ (\alpha(r) \beta(r) - \beta(r) \alpha(r)) \right], \quad (59)
\end{align*}
\]

\[
\begin{align*}
\psi^{111}_{\Gamma_1 = A_1}(r, r) &= \frac{1}{\sqrt{2}} \left[ \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) - \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) \right] \\
&\times \alpha(r) \alpha(r), \quad (60)
\end{align*}
\]

\[
\begin{align*}
\psi^{100}_{\Gamma_2 = B_2}(r, r) &= \frac{1}{\sqrt{2}} \left[ \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) - \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) \right] \\
&\times \frac{1}{\sqrt{2}} \left[ (\alpha(r) \beta(r) + \beta(r) \alpha(r)) \right], \quad (61)
\end{align*}
\]

\[
\begin{align*}
\psi^{100}_{\Gamma_3 = B_1}(r, r) &= \frac{1}{\sqrt{2}} \left[ \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) - \psi_{\xi \gamma}(r) \psi_{\gamma z}(r) \right] \\
&\times \beta(r) \beta(r). \quad (62)
\end{align*}
\]

In order to properly describe the energy of the anisotropic quadrupole interaction of Eq. (56), we calculate the quadrupole interaction energy of the Hamiltonian \(H_{0Q}(\gamma)\) of Eq. (46) in terms of the matrix representation for the two-electron states \(\psi^{\Gamma S S_z}_1(r, r)\) of Eqs. (57)-(62).

\[
H_{0Q}(\gamma) = -\sum_{\ell < j} \mathcal{J}^j_{\ell Q} \psi^{\ell}_{\ell \alpha_1}(r, r), \quad (63)
\]

Here, the quadrupole interaction energy of \(\mathcal{J}^j_{\ell Q}\) between electrons at positions \(r_1\) and \(r_2\) is calculated in terms of the radial function \(f_{\ell Q}(r)\) for the 3d electron in Eqs. (12) and (13) as

\[
\begin{align*}
\mathcal{J}^{11}_{\ell Q} &= \left( \frac{\sqrt{3}}{7} \right)^2 \int dr^2 dr^2 J_0(r, r_0) f_{\ell Q}(r)^2 f_{\ell Q}(r)^2 \\
&+ \frac{3}{49} \int dr^2 dr^2 J_0(r, r_0) f_{\ell Q}(r)^2 f_{\ell Q}(r)^2 \\
&\times (r - r_0)^2 f_{\ell Q}(r') f_{\ell Q}(r')^2. \quad (64)
\end{align*}
\]

In the integral in the lower line in Eq. (64), we take coordinates \(r, r'\) instead of \(r_1 = r - R, r_2 = r' - R\), for the positions \(R_1\) and \(R_2\) of \(d_{Fe}^2 + \cdots, \text{i.e., } R_1 = R_2\), or \(R_1 \neq R_2\). It is expected that the intra-atomic quadrupole interaction \(J_{\ell Q}^{12}\) for \(R_1 = R_2\), which is mostly independent of the lattice structure, will show isotropic azimuth angle dependence. This almost isotropic feature of the quadrupole interaction of \(J_{\ell Q}^{12}\) dominated by the intra-atomic coupling favors the \(s\)-like superconducting energy gap of the present iron pnictide. This will be discussed in Sect. 4.9.

Ultrasonic measurements under pulsed magnetic fields of up to 62 T reveal increases of 7.4% for the softened \(C_{66}\) at 84 K in the tetragonal phase of \(x = 0.036\) and 3.3% for the softened \(C_{66}\) at 30 K in the normal phase of \(x = 0.071\). Taking into account the robustness of the softening of \(C_{66}\) against magnetic fields in the normal phase above the structural and superconducting transition temperatures, we adopt the two-electron states of the Slater determinant with the spin-singlet states of Eqs. (57)-(59), but disregard those with the spin-triplet states of Eqs. (60)-(62). We abbreviate the two-electron state with the spin singlet of \(\psi^{000}_{\Gamma_1}(r, r)\) in Eqs. (57)-(59) to \(\psi^{000}_{\Gamma_1}(r, r)\) in the following discussion.

In the case of the highly anisotropic quadrupole interaction with \(\gamma = 0\), the quadrupole interaction energies of the \(\psi^{000}_{A_1}(r, r)\) and \(\psi^{000}_{B_2}(r, r)\) states in Eq. (63) causes the degeneration of each other and the energy of the \(\psi^{000}_{B_2}(r, r)\) state deviates from them. This highly anisotropic case of \(\gamma = 0\) in Eq. (46) leads to the ferro-quadrupole ordering of \(O_{\xi \gamma \gamma}^{\Gamma}\) accompanying the structural transition. With increasing the Co concentration \(x\) to the QCP of \(x_{\text{QCP}} = 0.061\), the quadrupole interaction of Eq. (46) develops an almost isotropic feature with \(\gamma \lesssim 1\), where the energies of the \(\psi^{000}_{B_2}(r, r)\) and \(\psi^{000}_{B_2}(r, r)\) states get closer to each other and the energy of the \(\psi^{000}_{A_1}(r, r)\) state is different. Since the quadrupoles \(O_{\xi \gamma \gamma}^{\Gamma}\) of Eq. (17) and \(O_{\xi \gamma \gamma}^{\Gamma}\) of Eq. (15) and the angular momentum \(l_z\) of Eq.
(16) obey the commutation relation of Eq. (18) among the Pauli matrices, we expect quantum fluctuation between the quadrupoles \( Q_{x'y'} \) and \( Q_{z'z'} \) in the vicinity of the QCP, which is particularly important for explaining the superconductivity accompanying the hexadecapole ordering. The special case of \( \gamma = 1 \) mapped on the ideal \( xz' \) model leads to the fully degenerate \( \psi_B(r, r_1) \) and \( \psi_B(r, r_j) \) states, which causes the disappearance of the hexadecapole. This is inconsistent with the experimental observation of the critical slowing down around the superconducting transition temperature.

When the rotation \( \omega_{xy} \) is induced by either the thermally excited transverse acoustic phonons or the experimentally generated transverse ultrasonic waves, the phases of the two-electron state of \( \psi_{\Gamma_1}(r, r) \) at positions \( r_1 \) and \( r_j \) in Eq. (56) bound by the quadrupole interaction of Eq. (46) are simultaneously changed by the rotation operator as follows:

\[
\psi_{\Gamma_1}(r, r_j) \rightarrow \exp \left[ -i\tilde{\omega}_{xy}(r) \right] \exp \left[ -i\tilde{\omega}_{xy}(r_j) \right] \times \psi_{\Gamma_1}(r, r_j).
\]

Thus, an infinitesimal amount of rotation \( \omega_{xy} \) perturbs the quadrupole interaction Hamiltonian of Eq. (46) as

\[
\left\{ \Gamma_1, H_{QO}(\omega_{xy}) \right\}_{\Gamma_1} = \int dr dr_j \psi_{\Gamma_1}^* (r, r_j) \exp \left[ i \left[ \hat{A}_x(r) + \hat{A}_y(r) \right] \right] \times H_{QO}(\gamma) \exp \left[ -i \left[ \hat{A}_x(r) + \hat{A}_y(r) \right] \right] \psi_{\Gamma_1}(r, r_j) \\
+ \int dr dr_j \psi_{\Gamma_1}^* (r, r_j) \left[ \hat{A}_x(r) + \hat{A}_y(r), H_{QO}(\gamma) \right] \times \psi_{\Gamma_1}(r, r_j) \omega_{xy} \\
+ \int dr dr_j \psi_{\Gamma_1}^* (r, r_j) \left[ \hat{A}_x(r) + \hat{A}_y(r), H_{QO}(\gamma) \right] \times \psi_{\Gamma_1}(r, r_j) \omega_{xy}^2.
\]

Using the commutation relation of Eq. (18) for the Pauli matrices, we reduce the perturbation Hamiltonian \( H_{\text{tot}}(\omega_{xy}) \) which depends on the rotation \( \omega_{xy} \) as follows:

\[
H_{\text{tot}}(\omega_{xy}) = 2(1 - \gamma) \sum_{i \neq j} J_{Q}(r_i - r_j) \\
\times \left[ O_{xy}(r) O_{y'x'}(r) + O_{x'y'}(r) O_{xy}(r) \right] \omega_{xy}^2
\]

\[
+ 4(1 - \gamma) \sum_{i \neq j} J_{Q}(r_i - r_j) \\
\times \left[ O_{y'z'}(r) O_{z'y'}(r) - O_{xy}(r) O_{xy}(r) \right] \omega_{xy}^2.
\]

From the first term in Eq. (67), which linearly depends on the rotation \( \omega_{xy} \), we identify the electric hexadecapole as

\[
H_{\text{H}^6}(r_1, r_j) = O_{xy}(r) O_{y'x'}(r) + O_{x'y'}(r) O_{xy}(r).
\]

The hexadecapole \( H_{\text{H}^6}(r_1, r_j) \) of Eq. (68) is invariant upon the exchange of positions \( r_1 \) and \( r_j \) but is antisymmetric upon the exchange of coordinates \( x' \) and \( y' \). In Fig. 5(c), we schematically show the interaction between the hexadecapole \( H_{\text{H}^6}(r, r_j) \) of Eq. (68) carried by the two-electron states and the rotation \( \omega_{xy} \) of the transverse acoustic phonons. The hexadecapole \( H_{\text{H}^6}(r_1, r_j) \) operates on the two-electron state that is bound by the quadrupole interaction of Eq. (46), while the hexadecapole \( H_{\text{H}^6}(r') \) in Eq. (23) acts on the one-electron state that is trapped in the CEF Hamiltonian of the central force. Note that the hexadecapole \( H_{\text{H}^6}(r, r_j) \) and rotation \( \omega_{xy} \) commonly belong to the \( A_2 \) symmetry of the point group symmetry \( D_{2d} \). The coefficient of the second term proportional to \( (\omega_{xy})^2 \) in Eq. (67) represents the energy modulation of the anisotropic quadrupole interaction.

Comparing the term proportional to the rotation \( \omega_{xy} \) in the expressions of Eq. (66) with that in Eq. (67), we write the Heisenberg equation of the time derivative for the total angular momentum \( \hat{L}(r, r_j) = \hat{L}(r) + \hat{L}(r_j) \) which is proportional to the hexadecapole \( H_{\text{H}^6}(r, r_j) \) as follows:

\[
\frac{\partial}{\partial t} \hat{L}(r, r_j) = \left[ \hat{L}(r, r_j), H_{QO}(\gamma) \right] = -2(1 - \gamma) J_{Q}(r_1 - r_j) H_{\text{H}^6}(r_1, r_j).
\]

Furthermore, the time derivative of the angular momentum in Eq. (69) is identified with the torque \( \tau_{\text{xy}}(r_1, r_j) \) for the two-electron state bound by the anisotropic quadrupole interaction of Eq. (46) as

\[
\hbar \frac{\partial}{\partial t} \hat{L}(r_1, r_j) = \tau_{\text{xy}}(r_1, r_j).
\]

Note that the torque \( \tau_{\text{xy}}(r_1, r_j) \) in Eq. (70) vanishes for the special case of the ideal isotropic quadrupole interaction with \( \gamma = 1 \) of Eq. (46) identified with the ideal \( xz' \) model. The hexadecapole \( H_{\text{H}^6}(r_1, r_j) \) proportional to the time derivative of the angular momentum in Eq. (69) conserves the time-reversal symmetry, while the angular momentum \( \hat{L}(r, r_j) \) itself breaks the time-reversal symmetry.

The hexadecapole-rotation interaction linearly coupled to the rotation \( \omega_{xy} \) in Eq. (67) has the following matrix elements for the two-electron states of \( \psi_{\Gamma_1}(r, r_j) \):

\[
\left\langle \Gamma_1, H_{\text{H}^6}(\omega_{xy}) \right\rangle_{\Gamma_1} = 2(1 - \gamma) \sum_{i \neq j} \int dr dr_j \psi_{\Gamma_1}^*(r, r_j) J_{Q}(r_i - r_j) H_{\text{H}^6}(r_1, r_j) \\
\times \psi_{\Gamma_1}(r, r_j) \omega_{xy}^2 \]

\[
= 2(1 - \gamma) \sum_{i \neq j} \int dr dr_j \psi_{\Gamma_1}^*(r, r_j) J_{Q}(r_i - r_j + r_f - R_j) \\
\times \psi_{\Gamma_1}(r, r_j) \omega_{xy}^2.
\]

In the integral of Eq. (71), we respectively take coordinates \( r \) and \( r_f \) instead of \( r_1 = r - R_i \) and \( r_f = r - R_f \). For the positions \( R_i \) and \( R_f \) of Fe\(^{2+}\) ions. As mentioned for Eq. (64), the intra-atomic quadrupole interaction between electrons accommodated in the same Fe\(^{2+}\) ion with \( R_i = R_f \) is dominant over the inter-atomic quadrupole interaction with \( R_i \neq R_f \). The hexadecapole formed by the intra-atomic quadrupole interaction
plays an important role in the appearance of the hexadecapole ordering in the superconducting state.

Among the two-electron states listed in Eqs. (57)-(62), we take the spin-singlet states consisting of the two-electron states $\psi_{A_1}(r_i, r_j)$ for the orbital symmetries of $\Gamma_v = A_1$, $B_2$, and $B_1$ compatible with the magnetic robustness of the present system, while we disregard the spin-triplet state of $\psi_{A_2}^{S=1, S_z=0}(r_i, r_j)$ with $S_z = 1, 0$, and $-1$. We deduce the hexadecapole-rotation interaction of Eq. (71) for the spin-singlet states as

$$H^{\omega}_{\text{red}}(\omega_{xy}) = -4(1 - \gamma) \sum_{i \neq j} J^l_Q \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \omega_{xy}. \quad (72)$$

Here, the matrix elements $\langle \Gamma_v' | H^{\omega}_{\text{red}}(\omega_{xy}) | \Gamma_v \rangle$ in Eq. (72) for the two-electron state $\psi_{\Gamma_v}(r_i, r_j)$ with the symmetries of $\Gamma_v = A_1$, $B_2$, and $B_1$ and the spin singlet of $S = 0$ of Eqs. (57)-(59) are calculated. The hexadecapole $H^{\omega}_{\text{red}}(r_i, r_j)$ with the $A_2$ symmetry possesses the off-diagonal elements between the two-electron states $\psi_{\Gamma_v}(r_i, r_j)$ and $\psi_{\Gamma_v'}(r_i, r_j)$, but these matrix elements vanish for the state $\psi_{A_1}(r_i, r_j)$. This is confirmed by the symmetry property of $B_2 \otimes B_1 = A_2$.

We have particular interest in the interplay of the rotation $\omega_{xy}$ with the appearance of the hexadecapole ordering and the superconductivity. Employing the unitary transformation for Eq. (72), we obtain the diagonal representation of the hexadecapole-rotation interaction as

$$H^{\omega}_{\text{red}}(\omega_{xy}) = -4 (1 - \gamma) \sum_{i \neq j} J^l_Q \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \omega_{xy}. \quad (73)$$

Here, we adopt the wave function $\psi_{\pm}(r_i, r_j)$ with $h = \pm$ for the two-electron states as

$$\psi_{\pm}(r_i, r_j) = \frac{1}{\sqrt{2}} \left[ \psi_{\Gamma_v}(r_i, r_j) \mp \psi_{\Gamma_v'}(r_i, r_j) \right] = \frac{1}{\sqrt{2}} \left[ \psi_{\pm}(r_i) \pm \psi_{\pm}(r_j) \right] \left( \psi_{\mp}(r_i) \mp \psi_{\mp}(r_j) \right) \times \frac{1}{\sqrt{2}} \left[ \alpha(r_i) \beta(r_j) - \beta(r_i) \alpha(r_j) \right]. \quad (74)$$

By analogy with the Zeeman term for the magnetic dipole moments in a magnetic field, we identify the wave function $\psi_{\pm}(r_i, r_j)$ with the eigenstate for the hexadecapole corresponding to the right-hand rotation of $h = +$ and the wave function $\psi_{\pm}(r_i, r_j)$ with the eigenstate for the hexadecapole corresponding to the left-hand rotation of $h = -$. The hexadecapole-rotation interaction of Eq. (73) indicates that the rotation $\omega_{xy}$ acts as a symmetry-breaking field on the hexadecapole carried by the two-electron states $\psi_{\pm}(r_i, r_j)$ and $\psi_{\pm}(r_i, r_j)$ of Eq. (74).

In order to properly describe the hexadecapole ordering, it is convenient to use the one-electron states $\lambda_{\pm}(r_i)$ described in terms of the spherical harmonics of $Y^n_l(\theta, \varphi)$ with the orbital quantum number $l = 2$ and the azimuthal quantum number $m = \pm 1$ and the radial part of $f_d(r_i)$ as

$$A_{\pm}(r_i) = f_d(r_i) Y^2_1(\theta_i, \varphi_i) = -\frac{1}{\sqrt{2}} \left[ i \psi_{\pm}(r_i) \pm \psi_{\mp}(r_i) \right]. \quad (75)$$

We rewrite the two-electron states $\psi_{\pm}(r_i, r_j)$ of Eq. (74) in terms of the one-electron wave function $\lambda_{\pm}(r_i)$ as

$$\psi_{\pm}(r_i, r_j) = \frac{1}{\sqrt{2}} \left[ e^{i\varphi_i} \lambda_{\pm}(r_i) \lambda_{\mp}(r_j) + e^{i\varphi_j} \lambda_{\mp}(r_i) \lambda_{\pm}(r_j) \right] \times \frac{1}{\sqrt{2}} \left[ \alpha(\theta_i) \beta(\varphi_i) - \beta(\theta_i) \alpha(\varphi_i) \right]. \quad (76)$$

Note that the eigenstates of $\psi_{\pm}(r_i, r_j)$ of Eq. (76) consist of the two-electron states of $\lambda_{\pm}(r_i) \lambda_{\mp}(r_j)$ and $\lambda_{\mp}(r_i) \lambda_{\pm}(r_j)$, which are superposed on each other while maintaining an orthogonal relation with a phase difference of $\pm 3\pi/2$.

Taking the spin-singlet state in Eq. (76) into account, we introduce annihilation operators of $B_1 \pm \sigma, \sigma'$ and creation operators of $B_1 \pm \sigma, \sigma'$ for the two-electron eigenstates $\psi_{\pm}(r_i, r_j)$ of the hexadecapole as

$$B_{i, \pm \sigma, \sigma'} = \frac{1}{\sqrt{2}} \left( e^{i\varphi_i} \lambda_{\pm}(r_i) \lambda_{\mp}(r_j) + e^{i\varphi_j} \lambda_{\mp}(r_i) \lambda_{\pm}(r_j) \right). \quad (77)$$

$$B_{i, \pm \sigma, \sigma'}^\dagger = \frac{1}{\sqrt{2}} \left( e^{i\varphi_i} \lambda_{\pm}(r_i) \lambda_{\mp}(r_j) + e^{i\varphi_j} \lambda_{\mp}(r_i) \lambda_{\pm}(r_j) \right). \quad (78)$$

Here, we use annihilation operators $l_{\pm \sigma, \sigma'}$ and creation operators $l_{\pm \sigma, \sigma'}^\dagger$ for the one-electron eigenstates $\lambda_{\pm}(r_i) \lambda_{\sigma}(r_j)$ of Eq. (75), which obey the following anticommutation relation for fermions:

$$[l_{i, \pm \sigma, \sigma' \lambda} \lambda_{j, \pm \sigma', \sigma'}], \quad (m, m' = \pm 1, \sigma, \sigma' = \uparrow \downarrow). \quad (79)$$

These electron operators are written in terms of $d_{i, \pm \sigma}$ and $d_{i, \pm \sigma}^\dagger$ of Eqs. (30) and (31) as

$$l_{i, \pm \sigma, \sigma'} = \frac{1}{\sqrt{2}} \left( id_{i, \pm \sigma}, \pm id_{i, \pm \sigma'} \right). \quad (80)$$

By using the two-electron operators of $B_{i, \pm \sigma, \sigma'}$ of Eq. (77) and $B_{i, \pm \sigma, \sigma'}^\dagger$ of Eq. (78), we rewrite the hexadecapole-rotation interaction $H^{\omega}_{\text{red}}(\omega_{xy})$ of Eq. (73) as

$$H^{\omega}_{\text{red}}(\omega_{xy}) = -4 (1 - \gamma) \sum_{i \neq j} J^l_Q H^{\omega}_{\text{red}}(\omega_{xy}). \quad (81)$$

Here, we describe the hexadecapole operator $H^{\omega}_{\text{red}}$ in terms of the difference between the occupation numbers $N_{i, \pm \sigma, \sigma'} = B_{i, \pm \sigma, \sigma'}^\dagger B_{i, \pm \sigma, \sigma'}$ of the two-electron state $\psi_{\pm}(r_i, r_j)$ and

$$N_{i, \pm \sigma, \sigma'} = B_{i, \pm \sigma, \sigma'}^\dagger B_{i, \pm \sigma, \sigma'} \psi_{\pm}(r_i, r_j) as$$

$$H^{\omega}_{\text{red}} = \frac{1}{2} \sum_{\sigma \neq \sigma'} \left( B_{i, \pm \sigma, \sigma'}^\dagger B_{i, \pm \sigma, \sigma'} - B_{i, \pm \sigma, \sigma'}^\dagger B_{i, \pm \sigma, \sigma'} \right) = \frac{1}{2} \sum_{\sigma \neq \sigma'} \left( N_{i, \pm \sigma, \sigma'} - N_{i, \pm \sigma, \sigma'} \right). \quad (82)$$

The two-electron wave function $\psi_{\pm}(r_i, r_j)$ of Eq. (74), consisting of a linear combination of $\psi_{\pm}(r_i, r_j)$ with the $B_2$ symmetry and $\psi_{\pm}(r_i, r_j)$ with the $B_1$ symmetry, possesses the hexadecapole with the $A_2$ symmetry of Eq. (82) in the diagonal
elements of Eq. (81). This is confirmed by the fact that the direct product of \( B_1 \oplus B_2 \) for the two-electron wave functions \( \psi_s(r_i, r_j) \) of Eq. (74) is reduced as \( (B_1 \oplus B_2) \oplus (B_1 \oplus B_2) = 2A_1 \oplus 2A_2 \) for the point group of the Fe\(^{2+}\) ion site.

Fourier transforms of the two-electron operators of \( B_{i,j,\pm,\sigma,\pi} \) of Eq. (77) and \( B^i_{j,\pm,\sigma,\pi} \) of Eq. (78) give their momentum representations. For example, the Fourier transform of \( B_{i,j,+,\sigma,\pi} \) is

\[
B_{i,j,+,\sigma,\pi} = \frac{1}{\sqrt{2}} \sum_{k, k_i} \left( e^{-i\frac{k}{2}l_{k_i-k_i}+1,\sigma} \langle \frac{l_{k_i-k_i}+1,\sigma}{k_i+k_i+1,\sigma} \rangle + e^{i\frac{k}{2}l_{k_i-k_i}+1,\sigma} \langle \frac{l_{k_i-k_i}+1,\sigma}{k_i+k_i+1,\sigma} \rangle \right) \times e^{i\mathbf{k}_0 \cdot \mathbf{r}_0/r_{k_i} r_{k_i}}. \tag{83}
\]

Here, we use the gravity position \( r_G = (r_i + r_j)/2 \) and gravity momentum \( \hbar r_G = \hbar \mathbf{k}_i + \hbar \mathbf{k}_j \). It is supposed that the two-electron states are described in terms of the coordinate \( r_k = r_i - r_j \) and relative momentum \( \hbar r_k = (\hbar \mathbf{k}_i - \hbar \mathbf{k}_j)/2 \) under the constraint that the gravity momentum vanishes as \( \hbar r_G = \hbar \mathbf{k}_i + \hbar \mathbf{k}_j = 0 \). Under this constraint, the motion of the two-electron state is explained only in terms of bound states with the relative momentum \( \hbar r_k = \hbar \mathbf{k} \). Consequently, the anihilation operators of \( B_{k,\pm,\sigma,\pi} \) for the eigenstates of the hexadecapole with the right-hand rotation of \( \hbar = + \) and the lefthand rotation of \( \hbar = - \) and the creation operators of \( B^i_{k,\pm,\sigma,\pi} \) for the conjugate eigenstates are written as

\[
B_{k,+,\sigma,\pi} = \frac{1}{\sqrt{2}} \left( e^{i\frac{k}{2}l_{k+1,\sigma}+1,\pi} \langle \frac{l_{k+1,\sigma}+1,\pi}{k+1,\sigma} \rangle + e^{-i\frac{k}{2}l_{k+1,\sigma}+1,\pi} \langle \frac{l_{k+1,\sigma}+1,\pi}{k+1,\sigma} \rangle \right),
\]

\[
B^i_{k,+,\sigma,\pi} = \frac{1}{\sqrt{2}} \left( e^{i\frac{k}{2}l_{k+1,\sigma}'-1,\pi} \langle \frac{l_{k+1,\sigma}'-1,\pi}{k+1,\sigma} \rangle + e^{-i\frac{k}{2}l_{k+1,\sigma}'-1,\pi} \langle \frac{l_{k+1,\sigma}'-1,\pi}{k+1,\sigma} \rangle \right). \tag{85}
\]

The two-electron operators of \( B_{k,+,\sigma,\pi} \) and \( B^i_{k,+,\sigma,\pi} \) given by Eqs. (84) and (85) satisfy the mixed commutation relations\(^{55}\)

\[
\begin{align*}
[B_{k,+,\sigma,\pi}, B^i_{k,+,\sigma,\pi}] &= \left( -\frac{n_{k+1,\sigma} - n_{k+1,\sigma} + n_{k-1,\pi} + n_{k-1,\pi}}{2} \right) \delta_{k,k'}, \tag{86} \\
[B_{k,+,\sigma,\pi}, B^i_{k',+,\sigma,\pi}] &= \pm i \delta_{n_{k+1,\sigma} - n_{k+1,\sigma} - n_{k-1,\pi} - n_{k-1,\pi}} \delta_{k,k'}. \tag{87}
\end{align*}
\]

Here, we denote the one-electron number operator as \( n_{k,+,\sigma} = \sum_{l_{k+1,\sigma} \pm 1,\pi} \). The mixed commutation relations of Eqs. (86) and (87) are required to calculate the hexadecapole interaction in the normal phase and describe the hexadecapole ordering associated with the superconducting transition at \( T_{SC} = 23 \) K for \( x = 0.071 \).

### 4.7 Hexadecapole interaction

In actual crystals of the iron pnictide, the thermally excited transverse acoustic phonon with wavevector \( q \) induces the rotation \( \omega_{xy}(q) \) as

\[
\omega_{xy}(q) = \frac{i}{2} \sqrt{\frac{\hbar}{2V_D \rho(q)}} q_i \langle \alpha_i, q - \alpha_i^+ \rangle. \tag{88}
\]

The two-electron states \( \psi_s(r_i, r_j) \) of Eq. (76) bearing the hexadecapole are scattered by the transverse acoustic phonons carrying the rotation \( \omega_{xy}(q) \). These scattering are expressed in terms of the hexadecapole-rotation interaction in momentum space as

\[
H_{\text{rot}}(\omega_{xy}) = -2(1 - \gamma) \sum_{k,q} J_0(k,q) \times \left( \frac{B^i_{k+q,+,\sigma,\pi} B_{k,+,-,\pi} - B^i_{k+q,-,-,\pi} B_{k,+,-,\pi}}{\omega_{xy}(q)} \right) = -4(1 - \gamma) \sum_{k,q} J_0(k,q) H^0_{\text{rot}}(\omega_{xy}(q)). \tag{89}
\]

The hexadecapole \( H^0_{\text{rot}} \) in Eq. (89) is written in terms of the two-electron state with wavevector \( k \) involving virtually excited one-phonon states with wavevector \( q \) as

\[
H^0_{\text{rot},k,q} = \frac{1}{2} \sum_{\sigma,\pi} H^0_{\text{rot},k,q,\sigma,\pi} = \frac{1}{2} \sum_{\sigma,\pi} \left( B^i_{k+q,+,\sigma,\pi} B_{k,+,-,\pi} - B^i_{k+q,-,\sigma,\pi} B_{k,+,-,\pi} \right). \tag{90}
\]

We identify the hexadecapole of Eq. (90) with the difference between the occupation numbers \( N_{k,+,-,\pi} = B^i_{k,+,-,\pi} B_{k,+,-,\pi} \) and \( N_{k,-,-,\pi} = B^i_{k,-,-,\pi} B_{k,+,-,\pi} \) for the two-electron states with the small-wavenumber limit of \( |q| \to 0 \) as follows:

\[
H^0_{\text{rot},k,q=0} = \frac{1}{2} \sum_{\sigma,\pi} H^0_{\text{rot},k,q=0,\sigma,\pi} = \frac{1}{2} \sum_{\sigma,\pi} \left( N_{k,+,-,\pi} - N_{k,-,-,\pi} \right). \tag{91}
\]

The canonical transformation involving the virtual one-phonon processes gives the indirect interactions between the two-electron states carrying the hexadecapole as\(^{45}\)

\[
H_{\text{ind}} = -\frac{1}{4} \sum_{k,k',q} \sum_{\sigma_1,\sigma_2} \sum_{\pi_1,\pi_2} D_{\pi_1 \pi_2}^{\pi_1 \pi_2} (k, q) \times \left( B^i_{k+q,+,\sigma_1,\pi_1} B_{k,+,-,\pi_1} B^i_{k',+,-,\sigma_2,\pi_2} B_{k,-,+,-,\pi_2} \right) + \frac{1}{4} \sum_{k,k',q} \sum_{\sigma_1,\sigma_2} \sum_{\pi_1,\pi_2} D_{\pi_1 \pi_2}^{\pi_1 \pi_2} (k, q) \times \left( B^i_{k+q,+,\sigma_1,\pi_1} B_{k,+,-,\pi_1} B^i_{k',+,\sigma_2,\pi_2} B_{k',+,-,\pi_2} \right) + \frac{1}{4} \sum_{k,k',q} \sum_{\sigma_1,\sigma_2} \sum_{\pi_1,\pi_2} D_{\pi_1 \pi_2}^{\pi_1 \pi_2} (k, q) \times \left( B^i_{k,-,-,\sigma_1,\pi_1} B_{k,+,-,\pi_1} B^i_{k',+,\sigma_2,\pi_2} B_{k',+,-,\pi_2} \right) + \frac{1}{4} \sum_{k,k',q} \sum_{\sigma_1,\sigma_2} \sum_{\pi_1,\pi_2} D_{\pi_1 \pi_2}^{\pi_1 \pi_2} (k, q) \times \left( B^i_{k,-,-,\sigma_1,\pi_1} B_{k,-,+,-,\pi_1} B^i_{k',+,-,\sigma_2,\pi_2} B_{k',+,-,\pi_2} \right). \tag{92}
\]

The indirect hexadecapole interaction Hamiltonian of Eq. (92) mediated by the rotation \( \omega_{xy}(q) \) of the transverse acous-
The sign of the interaction coefficient $D_H^{HH}(k, q)$ in Eq. (92) for the right-hand rotation direction of $h = +$ and the left-hand rotation of $h = -$ is expressed as

$$D_H^{HH}(k, q) = -\frac{1}{2} \left[ -4(1 - \gamma) J_0(k, q) \right]^2 \times \left\{ \frac{\hbar}{2V_{pbh}(q)^2} \left[ \epsilon_h(k) - \epsilon_i(k - q) \right]^2 - \hbar^2 \omega_i(q)^2 \right\},$$

with

$$h = \frac{4\hbar\omega_i(q)}{2V_{pbh}(q)^2} \left[ \epsilon_h(k) - \epsilon_i(k - q) \right]^2 - \hbar^2 \omega_i(q)^2 \right\} + \frac{h}{2V_{pbh}(q)^2} \left[ \epsilon_h(k) - \epsilon_i(k - q) \right]^2 - \hbar^2 \omega_i(q)^2 \right\}.$$\hspace{1cm} (93)

Here, $\epsilon_h(k) = \hbar^2 |k|^2 / 2m^*$ with effective mass $m^*$ for wavevector $k$ is the excitation energy of the two-electron states with the rotation direction of $h = \pm$ of Eq. (76). The transverse acoustic phonon energy $\hbar \omega_i(q)$ is $\hbar \nu_{66}q_i$ for $i = x$ or $y$ is given by the ultrasonic velocity $v_{66}$.

In the normal phase without long-range ordering, the energies of the two-electron states $\psi_+(r_i, r_j)$ and $\psi_-(r_i, r_j)$ cause the degeneration of each other as $\epsilon_+(k) = \epsilon_-(k) = \epsilon(k)$. By adopting the equality $D_H^{HH}(k, q) = D_H^{HH}(k, q)$, we deduce the indirect hexadecapole interaction between the two-electron states of Eq. (92) as

$$H_{\text{ind}}^{HH} = -\frac{1}{4} \sum_{k,k',q,r_i} \sum_{r_j} \sum_{\sigma_i, \sigma_j} \sum_{\sigma_i, \sigma_j} D_H^{HH}(k, q) \times \left( B_{k+q,r,r_i}^+ B_{k-r,-r_j,\sigma_i}^+ B_{k,-r,-r_j,\sigma_i}^- B_{k,-r,r_j,\sigma_j} \right) \times \left( B_{k+q,r,r_i}^+ B_{k-r,-r_j,\sigma_i}^+ B_{k,-r,-r_j,\sigma_j}^- B_{k,-r,r_j,\sigma_i} \right) \times \left( B_{k+q,r,r_i}^+ B_{k-r,-r_j,\sigma_i}^+ B_{k,-r,-r_j,\sigma_j}^- B_{k,-r,r_j,\sigma_i} \right) \times \frac{\hbar}{2V_{pbh}(q)^2} \left[ \epsilon(k) - \epsilon(k - q) \right]^2 - \hbar^2 \omega_i(q)^2 \right\},$$

with

$$H_{\text{ind}}^{HH}(k, q) = -\frac{1}{4} \sum_{k,k',q,r_i} \sum_{r_j} \sum_{\sigma_i, \sigma_j} \sum_{\sigma_i, \sigma_j} D_H^{HH}(k, q) \times \left\{ \frac{\hbar}{2V_{pbh}(q)^2} \left[ \epsilon(k) - \epsilon(k - q) \right]^2 - \hbar^2 \omega_i(q)^2 \right\},$$

This gives the boundary wavenumber $k_B^{HH} = m^* \nu_{66}/\hbar$, where the sign of $D_H^{HH}(k, q = 0)$ changes from positive to negative with increasing $|k|$. The experimental results in Fig. 1(a) for $x = 0.071$ give the ultrasonic velocity $v_{66}$ is 1750 m/s in the vicinity of the superconducting transition point $T_S = 23$ K ($v_{66} = 1970$ m/s at $T = 80$ K in the normal phase). From these results, we estimate the excitation energy of $\epsilon(k_B^{HH}) = \hbar^2 k_B^{HH}/2m^*$ to be 0.201 K (0.256 K) for the boundary wavenumber $k_B^{HH} = 34.0 \times 10^6$ m$^{-1}$ (30.2 $\times 10^6$ m$^{-1}$) and boundary wavelength $\lambda_B^{HH} = 0.185 \times 10^{-6}$ m (0.208 $\times 10^{-6}$ m). Here, we suppose that the two-electron states have an energy $\epsilon(k) = \hbar^2 |k|^2 / 2m^*$ with the effective mass being twice the rest electron mass $m^* = 2m_e$.

The low-lying two-electron state with the excitation energy $\epsilon_k(k) = \hbar^2 k_B^{HH}/2m^*$ is 0.25 K (5 GHz) contributes to the ferro-type hexadecapole interaction with the positive $D_H^{HH}(k, q = 0) > 0$. This brings about the ferro-hexadecapole ordering, which is actually confirmed by the critical slowing down around the superconducting transition temperature for $x = 0.071$ in Fig. 1(b). The hexadecapole interaction of $D_H^{HH}(k, q = 0)$ proportional to $(1 - \gamma)^2 J_0(k, q = 0)^2$ in Eqs. (95) and (96) determines the ferro-type hexadecapole transition temperature, as will be shown by Eq. (98) of Sect. 4.8.

### 4.8 Hexadecapole ordering

We use the hexadecapole susceptibility to describe the critical slowing down associated with the ferro-type hexadecapole ordering. According to the matrix representation of the hexadecapole-rotation interaction of Eq. (73), the right-hand rotation of $\omega_{xy} > 0$ splits the two-electron states of Eq. (76) into a lower level with $E_c = -4(1 - \gamma) J_0 \omega_{xy}$ for $\psi_+(r_i, r_j)$ with the right-hand rotation direction $h = +$ and an upper level with $E_c = 4(1 - \gamma) J_0 \omega_{xy}$ for $\psi_-(r_i, r_j)$ with the left-hand rotation direction $h = -$. The splitting of the two-electron states of $\psi_+(r_i, r_j)$ and $\psi_-(r_i, r_j)$ by the rotation $\omega_{xy}$ with the symmetry-breaking character illustrated in Fig. 7(b) gives the hexadecapole susceptibility $\chi_H$ for the two-electron state obeying the Curie law as

$$\chi_H = N_H \frac{16(1 - \gamma)^2 J_0^2 / C_6^0}{T} = \frac{\mu_H}{T}.$$\hspace{1cm} (97)
Here, \( N_2 \) is the number of two-electron states participating in the ferro-type hexadecapole interaction. The indirect hexadecapole-rotation interaction energy \( \Delta H \) in Eq. (97) is given by the hexadecapole interaction coefficient \( D^{HH} (k, q = 0) \) of Eq. (96) as

\[
\frac{2 \Delta H}{V N_H \rho_{M_{22}}^2} = \frac{32 (1 - \gamma^2) f_0^2}{V \rho_{M_{22}}^2} = \frac{1}{N_H} \sum |k| D^{HH} (k, q = 0) = D^{HH}.
\]

The positive sign in the indirect hexadecapole interaction coefficient \( D^{HH} \) due to \( \Delta H > 0 \) leads to the ferro-type hexadecapole ordering. Note that the softening of \( \rho_{M_{22}}^2 = C_{66} \) due to the quadrupole-strain interaction of Eq. (33) enhances the indirect hexadecapole interaction coefficient \( D^{HH} \) in Eq. (98).

The relaxation time \( \tau \) around the superconducting transition for \( x = 0.071 \) diverges at the critical temperature \( T^0 \) as shown in Fig. 4. Taking this experimental finding into account, we introduce the renormalized hexadecapole susceptibility \( \tilde{\chi}_H \) as

\[
\tilde{\chi}_H = \frac{\Delta H}{T - \Theta_c}.
\]

Here, we introduce the critical temperature \( \Theta_c \) corresponding to the experimentally observed critical temperature \( T^0 \) for \( \tau_H \). In the following Sects. 4.9 and 4.10, we present plausible model, where the hexadecapole ordering appears accompanying the superconductivity. Consequently, the critical temperature \( \Theta_c \) of Eq. (99) consists of the indirect hexadecapole interaction energy \( D^{HH} \) of Eq. (98) and the superconducting transition temperature \( T_{SC} \) as

\[
\Theta_c = \tilde{D}^{HH} + T_{SC}.
\]

Note that the superconducting transition temperature \( T_{SC} \) will be given later by the self-consistent equation for the superconducting energy gap of Eq. (121). The internal energy based on the phenomenological theory given by Eq. (141) in Sect. 4.10 also indicates the ground state for the simultaneous ordering of the hexadecapole and superconductivity in the present iron pnictide.

The critical slowing down of the relaxation time \( \tau_H \) is caused by the divergence of the correlation length associated with the ferro-type ordering of the hexadecapole \( H^c_r (r, r_j) \). This is expressed in terms of the renormalized hexadecapole susceptibility of Eq. (99) as

\[
\tau_H = \tau_0 \left| \frac{T - \Theta_c}{\Theta_c} \right|^{\gamma_\nu} = \tau_0 \left| \frac{T - \Theta_c}{\Theta_c} \right|^{-1} \propto \tilde{\chi}_H.
\]

The critical index \( \gamma_\nu = 1 \) of Eq. (101) based on mean field theory well reproduces the experimental results of the relaxation time \( \tau \) above the superconducting transition temperature \( T_{SC} \) in Fig. 1(b). Because the indirect hexadecapole interaction of Eq. (92) is mediated by the rotation of the transverse acoustic phonons with a long wavelength, the critical phenomena above the transition point is well described by mean field theory. The experimentally observed \( \gamma_\nu = 1/3 \) in the superconducting phase below \( T_{SC} \) in Fig. 1(b), however, distinctly deviates from \( \gamma_\nu = 1 \) of Eq. (101) obtained from mean field theory. This discrepancy is accounted for by the fact that the hexadecapole correlation due to the two-electron states develops in both the normal and superconducting phases near the transition temperature \( T_{SC} \), while the hexadecapole correlation due to the Cooper pairs develops only in the superconducting phase as will be shown in Sect. 4.10. The diffusion processes of the hexadecapole \( H^c_r (r, r_j) \) in the vicinity of the critical temperature \( \Theta_c \) determine the attempt relaxation time \( \tau_0 \) in Eq. (101).\(^{40,42}\) The calculation based on renormalization group theory for the inherent system exhibiting the hexadecapole ordering associated with the superconductivity may explains the experimental result of the critical index \( \gamma_\nu = 1/3 \) and the relative ratio \( \tau_0^\nu/\tau_0 = 1.03 \) for \( x = 0.071 \).

It is worth presenting the hexadecapole susceptibility responsible for the attenuation coefficient \( \alpha_{66} \) by comparing it with the quadrupole susceptibility responsible for the elastic constant \( C_{66} \) in Fig. 8. The critical slowing down due to the ferro-type hexadecapole ordering brings about the divergence of the relaxation time \( \tau_H \), which is expressed in terms of the renormalized hexadecapole susceptibility \( \tilde{\chi}_H \) of Eq. (99). As shown by the solid green line in Fig. 8, the divergence of the relaxation time \( \tau_H \) approaching the superconducting transition ensures the hexadecapole ordering at \( \Theta_c = T^0_H = T_{SC} = 23 \) K, consisting with the superconducting transition temperature. On the other hand, the elastic constant \( C_{66} \) shown by the red solid line in Fig. 8 exhibits softening obeying the renormalized quadrupole susceptibility \( \tilde{\chi}_Q \) in Eq. (51). The critical temperature \( T^0_H \) is \( \Theta_c + A_Q = -26.5 \) K, implying that the fictitious lattice instability temperature where \( C_{66} \to 0 \) is strictly distinguished from the critical temperature \( T^0_H = T_{SC} = 23 \) K for the divergence of the relaxation time \( \tau_H \). The critical slowing down due to the fictitious lattice instability may be possible, as indicated by the orange dashed and dotted line in
The ultrasonic attenuation due to the relaxation time $\tau_0$ at temperatures far above the fictitious instability point, however, is too small to detect.

The softening of $C_{66}$ in Fig. 8 is expressed in terms of the renormalized quadrupole susceptibility $\chi_0$ in Eq. (50), which is caused by the quadrupole-strain interaction of Eq. (33). The hexadecapole-rotation interaction of Eq. (73) might affect the softening of $C_{66}$ as

$$C_{66}^{\text{H}} = C_{66} (1 - \chi_0) = C_{66} \left(1 - \frac{\Delta H}{T - \Theta_C}\right).$$

Here, $C_{66}$ is given by Eq. (2) or Eq. (50) and represents the softening due to the quadrupole-strain interaction. Because two electrons are accommodated in the degenerate $yz$ and $xz$ bands, we take the number of two-electron states as $N_{1H} = (2N_{Fq})/2 = 2 \times 10^{22}$ cm$^{-3}$ as an upper limit. Adopting the quadrupole interaction energy $J_0 = \Theta_0 = -47$ K for $x = 0.071$ and the anisotropic parameter $\gamma = 0.9$ as a tentative value, we deduce that the hexadecapole-rotation interaction energy in Eq. (97) is as small as $\Delta H = 16N_{Fq}(1 - \gamma^2)J_0/C_{66} \sim 10^{-3}$ K. This is too small to sizably affect the softening of the elastic constant $C_{66}$. This small $\Delta H$ of $\sim 10^{-3}$ K is in strongly contrast to the considerable quadrupole-strain interaction energy of $\Delta H \sim 20$ K, which brings about appreciable softening of $C_{66}$ with decreasing temperature.

### 4.9 Superconductivity due to quadrupole interaction

In our attempt to show the superconducting state compatible with the hexadecapole ordering, we will solve the superconducting Hamiltonian for a pair of electrons coupled to each other through the quadrupole interaction $H_{QQ}(\gamma)$ of Eq. (46). To this end, we treat band electrons of the orbital state $\lambda_{\alpha}(r)$ in Eq. (75) with the angular momentum $l = 2$ and the azimuthal quantum number $m = \pm 1$. The corresponding bare electron Hamiltonian is expressed in terms of the electron operators of $l_{k,\sigma,\epsilon}$ and $l^\dagger_{k,\sigma,\epsilon}$ for $m = \pm 1$ as

$$H'_{k,\sigma} = \sum \sum \left[ \varepsilon_{k,\sigma}(\epsilon) l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} + c_{-\epsilon,\sigma}(\epsilon) l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} \right].$$

Here, the electron energy $\varepsilon_{m,\sigma}(\epsilon)$ is measured from the Fermi energy.

The quadrupoles expressed by the electron operators of $d_{l,\sigma}$ and $d^\dagger_{l,\sigma}$ ($l = yz$ and $xz$) in Eqs. (34) and (36) are rewritten in terms of the electron operators of $l_{k,\sigma,\epsilon}$ and $l^\dagger_{k,\sigma,\epsilon}$ with $m = \pm 1$ as

$$O_{xy,\sigma,\epsilon} = - i \sum_{\sigma} \left[l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} - l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} \right].$$

Thus, we obtain an alternative expression for the quadrupole interaction Hamiltonian $H_{QQ}(\gamma)$ with the anisotropic parameter $\gamma$ of Eq. (46) as

$$H_{QQ}(\gamma) = -\frac{1}{2} \sum \sum J_0(k, q) \left[l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} - l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} \right].$$

The quadrupole interaction $H_{QQ}(\gamma)$ of Eq. (106) gives four independent scattering processes between electrons with azimuthal quantum numbers of $m = +1$ and $-1$, wavevectors of $k$ an electron bearing the electric quadrupoles and $q$ of a transverse acoustic phonon, and spin orientations of $\sigma$ and $\sigma'$. In order to account for the critical slowing down around the superconducting transition point, we notice that the two scattering processes consisting of $l_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon}$ and $l^\dagger_{k,\sigma,\epsilon} l^\dagger_{k,\sigma,\epsilon}$ in Eq. (106) give the superconducting ground state bearing the hexadecapole. The former term of $l_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon}$ annihilates two electrons with the same azimuthal quantum number of $m = -1$ and creates two electrons with the same number of $m = +1$, while the latter term of $l_{k,\sigma,\epsilon} l^\dagger_{k,\sigma,\epsilon}$ causes the reverse process. On the other hand, we disregard the scattering of $l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon}$ and $l_{k,\sigma,\epsilon} l^\dagger_{k,\sigma,\epsilon}$ involved in exchange process from the electron state with $m = +1$ to the opposite state with $m = -1$, and that of $l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon}$ and $l_{k,\sigma,\epsilon} l^\dagger_{k,\sigma,\epsilon}$ for the exchange from $m = -1$ to $m = +1$. These latter scattering lead to a superconducting ground state that does not carry the hexadecapole, which is incompatible with the critical slowing down due to the hexadecapole ordering. Consequently, we adopt the restricted quadrupole interaction Hamiltonian consisting of the former process to properly describe the superconductivity accompanying the hexadecapole ordering:

$$H_{QQ}(\gamma) = -\frac{1}{2} \sum \sum J_0(k, q) \left[l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} - l^\dagger_{k,\sigma,\epsilon} l_{k,\sigma,\epsilon} \right].$$

Here, the gravity momentum for two-electron states bound by the restricted quadrupole interaction of Eq. (107) is constrained to vanish as $\hbar k_{\epsilon,\sigma} = 0$. Note that the restricted Hamiltonian $H_{QQ}(\gamma)$ of Eq. (107) satisfies the criterion of the $A_1$ symmetry of point group $D_{2d}$.

We solve the superconducting Hamiltonian $H_{SC}$ consisting of the bare electron Hamiltonian $H_{SC}'$ of Eq. (103) and the restricted quadrupole interaction Hamiltonian $H_{QQ}(\gamma)$ of Eq.
Here, the electron state vector of $l_k \equiv (l_{k,+1,\sigma \tau}, l_{k,+1,\tau \sigma}, l_{k,-1,\tau \sigma})^T$ is employed. We use the equivalence of the energy $\varepsilon_{+1,\sigma}(k) = \varepsilon_{-1,\sigma}(k) = \varepsilon(k)$ for the electrons with the azimuthal quantum numbers of $m = +1$ and $-1$. There are two different superconducting energy gaps of $\Delta^\tau_{+1,\sigma}(k)$ denoted by the Cooper pairs with the right-hand azimuthal quantum number $m = +1$ and $\Delta^\tau_{-1,\tau \sigma}(k)$ for the left-hand azimuthal quantum number $m = -1$ in Eq. (108) as

$$\Delta^\tau_{+1,\tau \sigma}(k) = \frac{1}{2}(1 - \gamma) \sum_q J_0(k,q) \langle l_{k,q+1,\sigma \tau}, l_{k,q+1,\tau \sigma} \rangle,$$  

$$\Delta^\tau_{-1,\tau \sigma}(k) = \frac{1}{2}(1 - \gamma) \sum_q J_0(k,q) \langle l_{k,q-1,\tau \sigma}, l_{k,q-1,\tau \sigma} \rangle.$$  

Here, $\langle l_{k,q-1,\tau \sigma}, l_{k,q-1,\tau \sigma} \rangle$ and $\langle l_{k,q-1,\tau \sigma}, l_{k,q-1,\tau \sigma} \rangle$ stand for the mean-field values of the Cooper pair indicating the off-diagonal long-range order parameter of the superconducting phase. The quadrupole interaction coefficient $J_0(k,q)$ and the anisotropic parameter $\gamma$ in Eq. (107) dominate the two energy gaps of $\Delta^\tau_{+1,\sigma}(k)$ in Eq. (109) and $\Delta^\tau_{-1,\tau \sigma}(k)$ in Eq. (110), which characterize the inherent superconductivity of the system. The appearance of the energy gap $\Delta^\tau_{+1,\tau \sigma}(k) \neq 0$ indicates the symmetry breaking of the U(1) gauge, where the electron number is not conserved across the superconducting transition.433

Supposing a Cooper pair consisting of two electrons with opposite spin orientations, we set the energy gap to $\Delta^\tau_{+1,\tau \sigma}(k) = \Delta^\tau_{-1,\tau \sigma}(k) = \Delta_{+1,\tau \sigma}(k)$ while omitting the spin orientations. The superconducting Hamiltonian $H_{\text{SC}}$ of Eq. (108) is expressed by Bogoliubov quasiparticles of $L_k \equiv (L_{k,+1,\tau \sigma}, L_{k,+1,\tau \sigma}, L_{k,-1,\tau \sigma}, L_{k,-1,\tau \sigma})^T$ as

$$H_{\text{SC}} = \sum_k \sum_{\tau \sigma} \left( \begin{array}{cccc} L_{k,+1,\tau \sigma}^T L_{k,+1,\tau \sigma} & L_{k,+1,\tau \sigma}^T L_{k,-1,\tau \sigma} & L_{k,-1,\tau \sigma}^T L_{k,+1,\tau \sigma} & L_{k,-1,\tau \sigma}^T L_{k,-1,\tau \sigma} \end{array} \right).$$  

Here, we obtain the excitation energies $\pm E_{+1}(k)$ and $\pm E_{-1}(k)$ of the Bogoliubov quasiparticles as

$$E_{+1}(k) = \sqrt{\varepsilon(k)^2 + \Delta_{+1,\tau \sigma}(k)^2}.$$  

Here, we adopt double-sign correspondence. The Bogoliubov transformation from the electron state vector of $l_k = (l_{k,+1,\tau \sigma}, l_{k,+1,\tau \sigma}, l_{k,-1,\tau \sigma}, l_{k,-1,\tau \sigma})^T$ to the Bogoliubov quasiparticles of $L_k = (L_{k,+1,\tau \sigma}, L_{k,+1,\tau \sigma}, L_{k,-1,\tau \sigma}, L_{k,-1,\tau \sigma})^T$ is expressed in terms of an unitary matrix as

$$\begin{pmatrix} l_{k,+1,\tau \sigma} \\ l_{k,+1,\tau \sigma} \\ l_{k,-1,\tau \sigma} \\ l_{k,-1,\tau \sigma} \end{pmatrix} = \begin{pmatrix} u_{+1}(k) & -v_{+1}(k) & 0 & 0 \\ v_{+1}(k) & u_{+1}(k) & 0 & 0 \\ 0 & 0 & u_{-1}(k) & -v_{-1}(k) \\ 0 & 0 & v_{-1}(k) & u_{-1}(k) \end{pmatrix} \begin{pmatrix} l_{k,+1,\tau \sigma} \\ l_{k,+1,\tau \sigma} \\ l_{k,-1,\tau \sigma} \\ l_{k,-1,\tau \sigma} \end{pmatrix}.$$  

Taking the constraint of $|u_{+1}(k)|^2 + |v_{+1}(k)|^2 = 1$ for fermion quasiparticles into account, we set the elements of the Bogoliubov transformation in Eq. (113) as

$$u_{+1}(k) = \frac{E_{+1}(k) + \varepsilon(k)}{\sqrt{[E_{+1}(k) + \varepsilon(k)]^2 + \Delta_{+1,\tau \sigma}(k)^2}},$$  

$$v_{+1}(k) = \frac{\Delta_{+1,\tau \sigma}(k)}{\sqrt{[E_{+1}(k) + \varepsilon(k)]^2 + \Delta_{+1,\tau \sigma}(k)^2}}.$$  

Here, $u_{+1}(k)$ is a real number and $v_{+1}(k)$ is a complex number. The Bogoliubov quasiparticles of $L_k$ in Eq. (111) obey the fermion commutation relations

$$\left[ L_{k,m,\tau \sigma}, l_{k,n,\tau \sigma}^\dagger \right] = \delta_{k,k'} \delta_{m,n} \delta_{\tau \sigma,\tau \sigma},$$  

$$\left[ L_{k,m,\tau \sigma}, l_{k,m',\tau \sigma}^\dagger \right] = 0.$$  

In the superconducting phase, the energy gaps of Eqs. (109) and (110) show finite values of $\Delta_{+1,\tau \sigma}(k) \neq 0$ and $\Delta_{-1,\tau \sigma}(k) \neq 0$ for both the ferro-type quadrupole interaction $J_0(k,q) > 0$ and the antiferro-type quadrupole interaction $J_0(k,q) < 0$. The slight deviation of the anisotropic feature of $\gamma \leq 1$ from the ideal $\chi_2$ model is necessary for the manifestation of the superconductivity in the vicinity of the QCP. The superconducting ground state $\Phi_0$ given by the restricted quadrupole interaction Hamiltonian of Eq. (107) is described in terms of the annihilation operators $L_{k,m,\tau \sigma}, l_{k,m,\tau \sigma}$ of the Bogoliubov
quasiparticles acting on the vacuum state $\Phi_{\text{vac}}$. An alternative expression for the superconducting ground state is obtained in terms of the electron creation operators $\hat{c}_{k \sigma \sigma}^\dagger$ of the Cooper pair acting on $\Phi_{\text{vac}}$. Consequently, the grand state $\Phi_0$ is expressed as

$$|\Phi_0\rangle = C \prod_{k} \prod_{m=0 \sigma \bar{\sigma}} \prod_{\sigma} L_{k,m,\sigma}^\dagger L_{k,m,\bar{\sigma}} |\Phi_{\text{vac}}\rangle,$$

$$= C \prod_{k} \prod_{m=0 \sigma \bar{\sigma}} \prod_{\sigma} \left[ -v_m(k) \right] \times \left[ u_m(k) + v_m(k) \right] |\Phi_{\text{vac}}\rangle. \quad (118)$$

Here, we take the available operations over the azimuthal quantum numbers of $m = +1$ and $-1$, spin orientations of $\sigma$ and $\bar{\sigma}$, and wavevector $k$. The coefficient of $C^{-2} = \prod_k \prod_{m=0 \sigma \bar{\sigma}} \prod_{\sigma} |v_m(k)|^2$ stands for the normalized factor of $\Phi_0$. The superconducting ground state $\Phi_0$ of Eq. (118) consists of the creation operators $\hat{c}_{k \sigma \sigma}^\dagger$ of the Cooper pairs with probability weight density $|v_m(k)|^2$ of Eq. (115). This is the coherent state treated in the standard BCS theory.\(^{46,84-86}\)

The restricted quadrupole interaction Hamiltonian of Eq. (107) brings about the energy gaps $\Delta_{l_{\pm1,\alpha \beta}} \neq 0$ of Eq. (109) and their complex conjugate energy gaps $\Delta^-_{l_{\pm1,\alpha \beta}} \neq 0$ of Eq. (110). The corresponding mean-field equations of the off-diagonal long-range order parameters of $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$ and $\langle \hat{c}_{k \sigma \sigma}^\dagger \hat{c}_{k \sigma \sigma} \rangle$ are written in terms of the Bogoliubov quasiparticles of Eq. (113) as

$$\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle = \langle \hat{c}_{k \sigma \sigma}^\dagger \hat{c}_{k \sigma \sigma} \rangle \left( 1 - \langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle \right)$$

$$- \langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle, \quad (119)$$

$$\langle \hat{c}_{k \sigma \sigma}^\dagger \hat{c}_{k \sigma \sigma} \rangle = \left( \langle \hat{c}_{k \sigma \sigma}^\dagger \hat{c}_{k \sigma \sigma} \rangle \right)^{-1}$$

$$- \langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle, \quad (120)$$

Here, we used the fact that the mean-field values for the off-diagonal excitation of $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$ and $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$ for the Bogoliubov quasiparticles vanish. The Bogoliubov quasiparticle numbers of $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$ and $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$ in Eqs. (119) and (120) are calculated in terms of the Fermi distribution function $f(E_{z_{\pm1}}(k)) = \left[ \exp \left[ E_{z_{\pm1}}(k) / k_B T \right] + 1 \right]^{-1}$ for the excitation energy $E_{z_{\pm1}}(k)$ in Eq. (112). By using the alternative expressions for the Bogoliubov-transform elements $|a_{\pm1}(k)|^2 = |v_{\pm1}(k)|^2$ and $2\epsilon_{\pm1}(k)v_{\pm1}(k) = \Delta_{l_{\pm1,\alpha \beta}}^\sigma(k) / E_{\pm1}(k)$, we obtain the self-consistent equation for the energy gap of Eq. (110) as

$$\Delta_{l_{\pm1,\alpha \beta}}^\sigma(k) = \frac{1}{2} \left( 1 - \gamma \right) \sum_q J_Q(k,q) \langle \hat{c}_{k \pm q,\alpha \beta} \hat{c}_{k \mp q,\alpha \beta} \rangle$$

$$= \frac{1}{4} \left( 1 - \gamma \right) \sum_q J_Q(k,q) \frac{\Delta_{l_{\pm1,\alpha \beta}}^\sigma(k + q)}{\sqrt{\epsilon(k + q)^2 + \Delta_{l_{\pm1,\alpha \beta}}^\sigma(k + q)^2}} \times \tanh \left[ \frac{\sqrt{\epsilon(k + q)^2 + \Delta_{l_{\pm1,\alpha \beta}}^\sigma(k + q)^2}}{2k_B T} \right]. \quad (121)$$

The quadrupole interaction $J_Q(k,q)$ and the anisotropic parameter $\gamma$ used in the restricted quadrupole interaction Hamiltonian $H_Q^\sigma(\gamma)$ of Eq. (107) dominate the self-consistent equation for the superconducting energy gaps of $\Delta_{l_{\pm1,\alpha \beta}}^\sigma(k)$ in Eq. (121). The microscopic mechanism for the Cooper pair formation in the present treatment is in good agreement with the previous theoretical studies based on the quadrupole interaction\(^{44-50}\) but are rather different from the theory based on the spin fluctuation.\(^{15,29,30}\) The superconducting transition temperature $T_{SC}$ determined by Eq. (121) in the present model and the hexadecapole interaction $D_{BB}^\chi$ of Eq. (98) both contribute to the critical temperature $\Theta_C$ of the renormalized hexadecapole susceptibility of Eq. (99) as $\Theta_C = D_{BB}^\chi + T_{SC}$ as shown in Eq. (100).

In order to characterize the superconducting state of the present iron pnictide, we calculate the eigenenergy of the restricted quadrupole interaction Hamiltonian $H_Q^\sigma(\gamma)$ of Eq. (107) for the superconducting ground state $\Phi_0$ of Eq. (118) as

$$\langle \Phi_0 | H_Q^\sigma(\gamma) | \Phi_0 \rangle = - \frac{1}{8} \sum_{k,q} J_Q(k,q) \frac{\Delta_{l_{\pm1,\alpha \beta}}^\sigma(k + q) \Delta_{l_{\pm1,\alpha \beta}}^\sigma(k) }{E_{+1}(k + q) - E_{-1}(k) }$$

$$+ \frac{\Delta_{l_{\pm1,\alpha \beta}}^\sigma(k + q) \Delta_{l_{\pm1,\alpha \beta}}^\sigma(k) }{E_{+1}(k + q) - E_{-1}(k) } \quad (122)$$

The antiferro- and ferro-quadrupole interactions of $J_Q(k,q)$ for various wavevectors $q$ of the transverse acoustic phonons over the Brillouin zone participate in the Cooper pair formation. However, a small-phonon number limit of $|q| \rightarrow 0$ corresponding to the measured ultrasonic wave particularly plays a significant role to cause the the critical slowing down due to the ferro-hexadecapole ordering. Therefore, we calculate the quadrupole interaction energy of $\langle \Phi_0 | H_Q^\sigma(\gamma) | \Phi_0 \rangle$ of Eq. (122) for the Cooper pairs bound by electrons with wavevectors $k$ and $k + q$ for the small-phonon number limit of $|q| \rightarrow 0$.

In our attempt to examine the interference between the phase $\varphi_{l_{\pm1,\alpha \beta}}(k)$ of the energy gap $\Delta_{l_{\pm1,\alpha \beta}}(k)$ due to the off-diagonal long-range order parameter $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$ and the phase $\varphi_{l_{\pm1,\sigma \bar{\sigma}}}(k)$ of $\Delta_{l_{\pm1,\alpha \beta}}(k)$ due to $\langle L_{k_{\pm1,\sigma \bar{\sigma}}k_{\pm1,\sigma \bar{\sigma}}} \rangle$, we take polar form of the energy gaps.

$$\Delta_{l_{\pm1,\alpha \beta}}(k) = |\Delta_{l_{\pm1,\alpha \beta}}(k)\rangle \exp \{ i \varphi_{l_{\pm1,\alpha \beta}}(k) \}. \quad (123)$$

Thus, we deduce the energy of the restricted quadrupole interaction of Eq. (107) for the superconducting ground state $\Phi_0$ in the small-phonon number limit of $|q| \rightarrow 0$ as

$$\langle \Phi_0 | H_Q^\sigma(\gamma) | \Phi_0 \rangle = - \frac{1}{8} \sum_{k} J_Q(k,0) \frac{\Delta_{l_{\pm1,\sigma \bar{\sigma}}}^\sigma(k) \Delta_{l_{\pm1,\alpha \beta}}^\sigma(k) }{E_{+1}(k) - E_{-1}(k) }$$

$$\times \cos \{ \varphi_{l_{\pm1,\alpha \beta}}(k) - \varphi_{l_{\pm1,\sigma \bar{\sigma}}}(k) \}. \quad (124)$$

The restricted quadrupole interaction energy of Eq. (124) depends on $\cos \{ \varphi_{l_{\pm1,\sigma \bar{\sigma}}}(k) - \varphi_{l_{\pm1,\alpha \beta}}(k) \}$ for the phase difference $\varphi_{l_{\pm1,\alpha \beta}}(k) - \varphi_{l_{\pm1,\sigma \bar{\sigma}}}(k)$ between the two energy gaps in Eq. (123).\(^{87}\) The Cooper pairs dominated by the ferro-type quadrupole interaction with $J_Q(k,0) > 0$ for the small-phonon regime of $|q| < q^0$ bring about the state for
cos [ϕ_{1,1}(k) − ϕ_{-1,-1}(k)] = 1 with the phase difference corresponding to the stationary point of ϕ_{1,1}(k) − ϕ_{-1,-1}(k) = sr for an even integer s = 2n. In the opposite case, however, the antiferro-type quadrupole interaction of J_0(k, 0) < 0, which is relevant for relatively high wavenumbers of |k| > K_0^2, has cos [ϕ_{1,1}(k) − ϕ_{-1,-1}(k)] = −1 with the stationary point of ϕ_{1,1}(k) − ϕ_{-1,-1}(k) = sr for an odd integer s = 2n + 1.

The indirect quadrupole interaction coefficient D^{SN}(k, q) of Eq. (41) in the Hamiltonian of Eq. (40) may possess positive or negative sign depending on the sign of its denominator. Since the coefficient D^{SN}(k, q) dominates the quadrupole interaction coefficient J_0(k, q), there are expected two cases of the ferro-type quadrupole interaction of J_0(k, q) > 0 and antiferro-type of J_0(k, q) < 0 in the restricted quadrupole interaction energy of Eq. (124). These both cases of J_0(k, q) > 0 and J_0(k, q) < 0 are commonly available for the superconducting Cooper pair formation in the system. The restricted quadrupole interaction H^{QQ}_0(γ) of Eq. (107) is ruled by the quadrupole interaction coefficient J_0(k, q) and the anisotropic coefficient γ ≤ 1 indicating the slight deviation from the ideal xz model. Consequently, the superconductivity energy gap caused by the restricted quadrupole interaction H^{QQ}_0(γ) is favorable for the s-like shape superconducting energy gap reflecting the almost isotropic feature in the x'y' plane.

4.10 Superconducting ground state and hexadecapole ordering

In order to examine the hexadecapole ordering in the superconducting phase, we investigate whether or not the superconducting ground state Φ_0 of Eq. (118) due to the restricted quadrupole interaction Hamiltonian H^{QQ}_0(γ) of Eq. (107) bears the hexadecapole. The annihilation operators B_{k,x,y,σ} of Eq. (84) and the creation operators B_{k,x,y,σ} of Eq. (85) describing the hexadecapole H^{Q}_{k,q} of Eq. (90) possess the following expectation values for the superconducting ground state Φ_0 of Eq. (118):

\[ \langle Φ_0 | B_{k,x,y,σ} | Φ_0 \rangle = \frac{1}{2} \sum_{x',y',σ'} \left[ e^{i q \cdot x'} B_{-1,-1}(k) + e^{i q \cdot y'} B_{1,1}(k) \right] \tag{125} \]

\[ \langle Φ_0 | B_{k,x,y,σ}^\dagger | Φ_0 \rangle = \frac{1}{2} \sum_{x',y',σ'} \left[ e^{i q \cdot x'} B_{-1,-1}(k) + e^{i q \cdot y'} B_{1,1}(k) \right] \tag{126} \]

The finite values of \langle Φ_0 | B_{k,x,y,σ} | Φ_0 \rangle ≠ 0 and \langle Φ_0 | B_{k,x,y,σ}^\dagger | Φ_0 \rangle ≠ 0 are expected with the appearance of the energy gaps A_{1,1}(k) ≠ 0 of Eq. (109) and A_{-1,-1}(k) ≠ 0 of Eq. (110) below the superconducting transition temperature. This result shows that the superconducting ground state Φ_0 of Eq. (118) actually bears the off-diagonal long-range order parameters B_{k,x,y,σ} and B_{k,x,y,σ} for the Cooper pairs.

The hexadecapole H^{Q}_{k,q} of Eq. (90) is expressed in terms of the difference in the numbers of Cooper pairs as

\[ H^{Q}_{k,q} = \frac{1}{2} \sum_{x,y,σ} \left( B_{k,x,y,σ}^\dagger B_{k,x,y,σ} - B_{k,x,y,σ} B_{k,x,y,σ}^\dagger \right) \]

\[ = \frac{i}{2} \sum_{σ,σ'} \left( \sum_{k,q} \left( (i B_{k+q,σ,σ'} B_{k,q,σ,σ'} - B_{k+q,σ,σ'}^\dagger B_{k,q,σ,σ'}) \right) \right) \tag{127} \]

Thus, we obtain the expectation value for the hexadecapole for the superconducting ground state Φ_0 as

\[ \langle Φ_0 | H^{Q}_{k,q} | Φ_0 \rangle = \frac{i}{4} \left( A_{-1,-1}(k) + B_{1,1}(k) \right) \frac{\Delta_{-1,-1}(k) \Delta_{1,1}(k)}{E_{-1}(k) - E_{1}(k)} \frac{\langle \omega_{xy} \rangle}{\omega_{xy}} \tag{128} \]

The appearance of the energy gaps A_{±1,1}(k) ≠ 0 in the superconducting phase simultaneously brings about a finite eigenvalue of the hexadecapole \langle Φ_0 | H^{Q}_{k,q} | Φ_0 \rangle ≠ 0.

The critical slowing down of the relaxation time τ_{rel} around the superconducting transition point in Fig. 1(b) is observed via the transverse ultrasonic waves with wavelengths as long as λ ~ 10 μm. Therefore, we treat the rotation ω_{xy} of the transverse acoustic phonons in Eqs. (127) and (128) for the small-wavenumber limit of |q| = 2π/λ → 0. Furthermore, we assume equivalence in the amplitudes of |A_{±1,1}(k)| = |A_{±1,1}(k)| for the two energy gaps of Eq. (109) and in the excitation energies of E_{1,1}(k) = E_{1,1}(k) = E(k) for the Bogoliubov quasiparticles of Eq. (113). The hexadecapole H^{Q}_{k,q} of Eq. (127) corresponding to the difference in the numbers of Cooper pairs N_{k,x,y,σ} and N_{k,-x,-y,σ} has an expectation value for the superconducting ground state Φ_0 of

\[ \langle Φ_0 | H^{Q}_{k,q=0} | Φ_0 \rangle = \left( \frac{1}{2} \sum_{σ,σ'} \left( (N_{k,x,y,σ} - N_{k,-x,-y,σ}) \right) \right) \frac{\langle \omega_{xy} \rangle}{\omega_{xy}} \tag{129} \]

Thus, the hexadecapole ordering corresponding to the finite difference in the numbers of Cooper pairs N_{k,x,y,σ} − N_{k,-x,-y,σ} leads to sin [ϕ_{1,1}(k) − ϕ_{-1,-1}(k)] ≠ 0 for the finite deviation of the phase difference of ϕ_{1,1}(k) − ϕ_{-1,-1}(k) from the stationary point of sr with an even integer s = 2n for J_0(k, 0) > 0 or with an odd integer s = 2n + 1 for J_0(k, 0) < 0. On the other hand, when the number of Cooper pairs N_{k,x,y,σ} is equivalent to the counter number of N_{k,-x,-y,σ}, we expect the equilibrium state of sin [ϕ_{1,1}(k) − ϕ_{-1,-1}(k)] = 0 in accordance with the phase difference located at the stationary point of ϕ_{1,1}(k) − ϕ_{-1,-1}(k) = 2πσ or (2n + 1)π.

The interaction of the hexadecapole H^{Q}_{k,q} with the rotation ω_{xy} of the transverse acoustic phonons of Eq. (89) generates a perturbation in the quadrupole interaction energy of Eq. (124) in the superconducting phase. The expectation value of the hexadecapole-rotation interaction Hamiltonian H_{rot}(ω_{xy}) of Eq. (89) for the superconducting ground state Φ_0 is calculated as

\[ \langle Φ_0 | H_{rot}(ω_{xy}) | Φ_0 \rangle = i (1 - γ) \sum_{k,q} J_0(k, q) \left[ \frac{A_{1,1}(k + q) A_{-1,-1}(k)}{E_{1}(k + q) - E_{-1}(k)} \right] \frac{\langle \omega_{xy} \rangle}{\omega_{xy}} \tag{130} \]
Since the rotation $\omega_{xy}(0)$ of the transverse acoustic phonons in the small-wavenumber regime of $|q| \to 0$ participates in the ferro-type hexadecapole interaction, the hexadecapole-rotation interaction energy $\langle \Phi_0 | H_{\text{rot}}(\omega_{xy}) | \Phi_0 \rangle$ in the superconducting state of Eq. (130) is reduced as

$$\langle \Phi_0 | H_{\text{rot}}(\omega_{xy}) | \Phi_0 \rangle = -2(1 - \gamma) \sum_k J_Q(k, q = 0) \frac{|\Delta(k)|^2}{E(k)^2} \times \sin[\varphi_{1,1}(k) - \varphi_{-1,-1}(k)] \omega_{xy}(0)$$

$$= -4(1 - \gamma) \sum_k J_Q(k, q = 0) \langle \Phi_0 | H_{\text{rot}}^{q,k \neq 0} | \Phi_0 \rangle \omega_{xy}(0).$$

(131)

Here, we used the expectation value of the hexadecapole of Eq. (129) for the superconducting ground state $\Phi_0$ of Eq. (118). As discussed for Eqs. (69) and (70), the torque $\tau_{xy}(r, r')$ is proportional to the hexadecapole. It is meaningful to show the expectation value of the torque $\tau_{xy}$ for the superconducting ground state $\Phi_0$ as follows:

$$\langle \Phi_0 | \tau_{xy} | \Phi_0 \rangle = -4(1 - \gamma) \sum_k J_Q(k, q = 0) \langle \Phi_0 | H_{\text{rot}}^{q,k \neq 0} | \Phi_0 \rangle \omega_{xy}(0).$$

(132)

Thus, we have an elementary expression for the hexadecapole-rotation interaction energy in terms of the torque $\tau_{xy}$ and rotation $\omega_{xy}(q = 0)$ as

$$\langle \Phi_0 | H_{\text{rot}}(\omega_{xy}) | \Phi_0 \rangle = \langle \Phi_0 | \tau_{xy} | \Phi_0 \rangle \omega_{xy}(0).$$

(133)

Note that the expectation value of the torque $\langle \Phi_0 | \tau_{xy} | \Phi_0 \rangle$ defined in Eq. (132) spontaneously becomes finite with the appearance of the hexadecapole ordering $\langle \Phi_0 | H_{\text{rot}}^{q,k \neq 0} | \Phi_0 \rangle \neq 0$ due to the superconducting energy gaps of $|\Delta_{1,1}(k)| - |\Delta_{-1,-1}(k)| \neq 0$ in the superconducting phase.

In order to specify the hexadecapole ordering in the superconducting phase far below the transition temperature, we adopt a phenomenological treatment using the microscopic theory described above. The internal energy $U$ includes both the restricted quadrupole interaction energy of Eq. (124) and the hexadecapole-rotation interaction energy for the rotation $\omega_{xy}(0)$ in the small-wavenumber limit of $|q| \to 0$ in Eq. (130) as

$$U = \sum_k U(k)$$

$$= -\frac{1}{2}(1 - \gamma) \sum_k J_Q(k, 0) \frac{|\Delta(k)|^2}{E(k)^2} \times [\cos[\varphi_{1,1}(k) - \varphi_{-1,-1}(k)] + 4 \sin[\varphi_{1,1}(k) - \varphi_{-1,-1}(k)] \omega_{xy}(0)]$$

$$+ \frac{1}{2} C_{66}^0 \omega_{xy}(0)^2 + \frac{1}{4} \beta \omega_{xy}(0)^4.$$

(134)

Here, we adopt the harmonic rotation energy of $C_{66}^0 \omega_{xy}(0)^2 / 2$ and the higher-order term of $\beta \omega_{xy}(0)^4 / 4$ with $\beta > 0$ to avoid instability of the system. Since the present system has the spin-singlet property of $S = 0$, we take the sum of the spin orientation as $\sum_{\sigma = \sigma'} = 2$ in the internal energy $U$ of Eq. (134). We seek the minimum of the internal energy $U(k)$ of Eq. (134) in finite variations of the phase difference of $\delta \varphi(k) = \varphi_{1,1}(k) - \varphi_{-1,-1}(k) - \pi \neq 0$ from the stationary point of $\pi = 2\pi$ for the ferro-type quadrupole interaction of $J_Q(k, 0) > 0$ or $\pi = (2n + 1)\pi$ for the antiferro-type quadrupole interaction of $J_Q(k, 0) < 0$ and the finite rotation $\omega_{xy}(0) \neq 0$.

The internal energy $U(k)$ characterized by wavevector $k$ in Eq. (134) is expanded up to the second order of $\delta \varphi(k)$ as

$$U(k) = -\frac{1}{2}(1 - \gamma) J_Q(k, 0) \cos(\pi) \frac{|\Delta(k)|^2}{E(k)^2} \times [1 - \frac{1}{2} \delta \varphi(k)^2 + 4 \delta \varphi(k) \omega_{xy}(0)]$$

$$+ \frac{1}{2} C_{66}^0 \omega_{xy}(0)^2 + \frac{1}{2} \beta \omega_{xy}(0)^4.$$

(135)

Here, $N_C = \sum_k$ is the number of Cooper pairs participating in the superconductivity. For simplicity, we use the abbreviated notation $S_Q(k)$ proportional to the square of the energy gap $|\Delta(k)|^2$ as

$$S_Q(k) = \frac{1}{2}(1 - \gamma) J_Q(k, 0) \cos(\pi) \frac{|\Delta(k)|^2}{E(k)^2}$$

$$= \frac{1}{2}(1 - \gamma) J_Q(k, 0) \frac{|\Delta(k)|^2}{E(k)^2}.$$

(136)

Since the quadrupole interaction of $J_Q(k, 0)$ is dominated by the indirect quadrupole interaction of $D_{4s}^0(0)$ of Eq. (42), the ferro-type quadrupole interaction of $J_Q(k, 0) > 0$ for the small-wavenumber regime of $|k| < k^Q_b$ causes the energy gaps with the phase difference around the stationary point of $\pi = 2\pi$ for $\cos(2\pi) = 1$, while the antiferro-type interaction of $J_Q(k, 0) < 0$ with the relatively large-wavenumber regime of $|k| > k^Q_b$ brings about the energy gaps with the phase difference around the stationary point of $\pi = (2n + 1)\pi$ for $\cos((2n + 1)\pi) = -1$. The experimentally determined phase diagram as shown in Fig. 4 indicates that the ferro-type quadrupole interaction for the $C$ concentration $x$ below the QCP of $x_{\text{QCP}} = 0.061$ changes to the antiferro-type quadrupole interaction with increasing $x$ across $x_{\text{QCP}}$. Therefore, the inherent property, that both the antiferro- and ferro-quadrupole interactions participate in the Cooper pair formation in Eq. (136), is available for the appearance of the superconductivity in the vicinity of the QCP.

Thus, the internal energy $U(k)$ of Eq. (135) is deduced as

$$U(k) = \frac{1}{2} S_Q(k) [\delta \varphi(k) - 4 \omega_{xy}(0)]^2$$

$$+ \frac{1}{4} \beta \frac{1}{4} \left[ \frac{1}{2} \omega_{xy}(0)^2 - \frac{1}{2} \left[ S_Q(k) - \frac{1}{16} \frac{C_{66}^0}{N_C} \right]^2 \right]$$

$$- S_Q(k) - \frac{1}{16} \frac{C_{66}^0}{N_C} \left[ S_Q(k) - \frac{1}{16} \frac{C_{66}^0}{N_C} \right]^2.$$

(137)

The appearance of the energy gap $|\Delta(k)| \neq 0$ in the superconducting phase leads to a finite value of $S_Q(k) \neq 0$ in Eq. (136). The minimum of the internal energy $U(k)$ of Eq. (137) is satisfied by the following constraint for the phase deviation.
of $\delta \varphi (k)$:

$$\delta \varphi (k) = 4 \omega_{xy} (0).$$

(138)

This result means that the finite phase deviation of $\delta \varphi (k) = \varphi_{x1+1} (k) - \varphi_{x-1+1} (k) - \pi / \alpha \neq 0$ from the stationary point of $\pi / \alpha = 2(n+1) \pi$ associated with the hexadecapole ordering brings about the spontaneous rotation of $\omega_{xy} (0) \neq 0$ in the superconducting state.

The energy $U(k)$ of Eq. (137) is optimized by the spontaneous rotation $\omega_{xy} (0)$ as

$$\omega_{xy} (0) = \pm 4 \frac{N_c}{\beta} \left[ S_Q (k) - \frac{1}{16} \frac{C_{66}^0}{N_c} \right].$$

(139)

Here, we need the criterion

$$S_Q (k) - \frac{1}{16} \frac{C_{66}^0}{N_c} > 0.$$ 

(140)

When the appropriate magnitude of $S_Q (k)$ due to the superconducting energy gap $\delta \varphi (k)$ in Eq. (136) satisfies the criterion of Eq. (140), the spontaneous rotation $\omega_{xy} (0) \neq 0$ of Eq. (139) of the macroscopic superconducting state occurs with respect to the host lattice. The occurrence of the spontaneous rotation $\omega_{xy} (0) \neq 0$ gives the optimized internal energy associated with the superconductivity bearing the hexadecapole as

$$U_H (k) = - \frac{64}{N_c} \frac{C_{66}^0}{\beta} \left[ S_Q (k) - \frac{1}{16} \frac{C_{66}^0}{N_c} \right]^2.$$ 

(141)

The first term $-S_Q (k)$ in Eq. (141) is the restricted quadrupole interaction energy with the null phase difference of $\delta \varphi (k) = \varphi_{x1+1} (k) - \varphi_{x-1+1} (k) - \pi / \alpha = 0$ corresponding to $\cos [\varphi_{x1+1} (k) - \varphi_{x-1+1} (k)] = 1$ for the stationary point of $\pi / \alpha = 2(n+1) \pi$ in Eq. (124).

The hexadecapole ordering of $\langle H_{z}^2 \rangle \neq 0$ due to the spontaneous deviation $\delta \varphi (k) \neq 0$ from the stationary rotational point of $\pi / \alpha = 2(n+1) \pi$ leads to the spontaneous rotation $\omega_{xy} (0) \neq 0$ with respect to the container of the host lattice. According to the second term in Eq. (141), the spontaneous rotation $\omega_{xy} (0) \neq 0$ further lowers the internal energy $U(k)$ from the stationary energy $-S_Q (k)$ of the restricted quadrupole interaction for the superconducting ground state of Eq. (118). In the framework of the phenomenological theory for the second-order transition, the quenching of the pair-electron state with the $A_2$ symmetry of the higher-symmetry group $D_{4h}^{25}$ associated with the spontaneous rotation $\omega_{xy} (0) \neq 0$ brings about a twisted phase with the lower-symmetry space group $C_{4h}^{25}$. The spontaneous breaking of the $A_2$ symmetry associated with $\langle H_{z}^2 \rangle \neq 0$ and $\omega_{xy} (0) \neq 0$ loses the symmetry operations consisting of $2C_{2z \pi}^2, 2C_{2z \pi}^2, 2C_{2z \pi}^2$, and $2C_{2z \pi}^2$ in the space group $D_{4h}^{25}$ of the mother phase. Consequently, the macroscopic superconducting state spontaneously twists by $\omega_{xy} (0) \neq 0$ with respect to the host lattice. The hexadecapole of Eq. (68) is carried by the two-electron states of Eq. (74), which consist of two electrons accommodated in the degenerate $\gamma z$ and $\gamma x'$ band orbitals mapped on the special unitary group SU(2). Therefore, the appearance of the hexadecapole ordering $\langle H_{z}^2 \rangle \neq 0$ of Eq. (129) is explained by the symmetry breaking in the direct product of the special unitary group SU(2)$ \otimes$ SU(2).

The critical slowing down in the relaxation time $\tau_H$ observed via the ultrasonic attenuation coefficient $\alpha_{66}$ of the transverse ultrasonic wave around the superconducting transition is explained in terms of the hexadecapole susceptibility for the ferro-type ordering of the hexadecapole $H_{z}^6$. The finite expectation value of the hexadecapole $H_{z}^6$ of Eq. (129) means that the superconducting ground state of Eq. (118) actually bears the hexadecapole. This result convincingly accounts for why the critical slowing down due to the hexadecapole ordering is observed around the superconducting transition. The direct detection of the spontaneous rotated state $\omega_{xy} (0) \neq 0$ due to the hexadecapole ordering in the superconducting phase is strongly required in future.

As is presented in Fig. 1(b), the onset of the critical slowing down in the relaxation time $\tau_H$ appears in the normal phase far above the superconducting transition temperature of $T_{SC}$ = 23 K, where fermion quasiparticles are relevant but the off-diagonal long-range ordering of the Cooper pairs does not exist. This means that the hexadecapole $H_{z}^6$ of Eq. (90) in the normal phase is actually carried by the fermion quasiparticles but not by the Cooper pairs. The indirect hexadecapole interaction $D_{10}^{ij}(\mathbf{k}, \mathbf{q})$ of Eq. (95) between two-electron states mediated by the rotation $\omega_{xy} (q)$ of the transverse acoustic phonons with the small-wavenumber limit of $|q| \rightarrow 0$ favors the ferro-type hexadecapole ordering. This ferro-type hexadecapole interaction reduces the energy of the two-electron states bearing the hexadecapole in both normal and superconducting phases. This plausibly explains why the system specially favors the Cooper pairs bearing the hexadecapole among the various types of Cooper pairs due to the quadrupole interaction of Eq. (106).

The indirect hexadecapole interaction Hamiltonian of Eq. (94) responsible for the hexadecapole ordering of $H_{z}^6$ is mapped to the Ising model. The critical index of $\gamma \tau = 1$ determined by the relaxation time $\tau_H$ in the normal phase above the superconducting transition temperature for $x = 0.071$ is in good agreement with mean field theory and reasonable consistent with the three-dimensional Ising model with $\gamma \tau = 1.2$ for $\nu = 0.63$ and $\nu = 2.04$. The critical index of $\gamma \tau = 1 / 3$ in the superconducting phase below $T_{SC}$, however, considerably deviates from the standard scaling theory with the same critical indices in both the normal and ordered phases. This inconsistency of $\gamma \tau = 1 / 3$ below $T_{SC}$ and $\gamma \tau = 1$ above $T_{SC}$ is accounted for by the inherent properties of the present system where the superconductivity and the hexadecapole ordering simultaneously appear.

The quenching of the $A_2$ symmetry of the hexadecapole ordering $\langle H_{z}^2 \rangle \neq 0$ accompanied the superconducting transition for $x = 0.071$ changes the symmetry of the mother tetragonal phase with the space group $D_{4h}^{25}$ to the ordered tetragonal phase with the space group $C_{4h}^{25}$, while the quenching of the $B_2$ symmetry of the quadrupole ordering $\langle O_{y6}\rangle \neq 0$ accompanied the structural transition for $x = 0.036$ gives the orthorhombic phase with the space group $D_{4h}^{25}$. Note that the space groups $C_{4h}^{25}$ for the hexadecapole ordered phase and $D_{4h}^{25}$ for the quadrupole ordered phase are subfamilies of the space group $D_{4h}^{25}$ for the mother tetragonal phase. The orthorhombic phase of the space group $D_{4h}^{25}$ due to the ferro-quadrupole ordering changes to the superconducting phase
below $T_{\text{SC}} = 16.4$ K for $x = 0.036$. The orthorhombicity of $\delta = (a-b)/(a+b) \sim 10^{-3}$ for the lattice parameters $a$ and $b$ in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x = 0.047-0.063$ reveals the tendency of $\delta \to 0$ with decreasing temperature in the superconducting phase.\(^{14}\) This reentrant property favoring the tetragonal lattice instead of the distorted orthorhombic lattice in the superconducting phase is consistent with the tetragonal structure $c^x_{4h}$ proposed as the hexadecapole ordering phase in the present paper. In short, we conclude that the unconventional superconductivity accompanying the hexadecapole ordering in the present system is a common feature across the QCP for $x = 0.061$.

5. Conclusion

In the present work, we investigated the order parameter dynamics around the superconducting and structural transitions in the iron pnictide Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ by means of ultrasonic measurements. The critical slowing down of the relaxation time $\tau$ due to freezing of the order parameter fluctuations associated with the superconducting and structural transitions was verified by the divergence of the ultrasonic attenuation coefficients. In the analysis of the experiments, we employed the significant fact that the transverse ultrasonic waves used to measure the elastic constant $C_{66}$ simultaneously induce the rotation $\omega_{xy}$ of the antisymmetric tensor and the strain $\varepsilon_{xy}$ of the symmetric tensor. Taking the band calculations on the iron pnictide into account, we suppose that the degenerate $\gamma'$ $z$ and $\chi'$ bands carrying the electric quadrupoles $O_{\chi',\gamma'}$ and $O_{\chi',\chi'}$ and the angular momentum $l$ play an essential role in the appearance of the superconducting and structural transitions in the system. We attempted to clarify the order parameters caused by the symmetry breaking of the space group $D_{4h}$ of the tetragonal mother phase and the special unitary group SU(2) of the degenerate $\gamma'$ $z$ and $\chi'$ bands.

The structural transition in the compound $x = 0.036$ is caused by the ferro-quadrupole ordering of $O_{\chi',\gamma'}$, which was identified as one of the generator elements of SU(2). The interaction of the quadrupole $O_{\chi',\gamma'}$ to the strain $\varepsilon_{xy}$ leads to a structural transition due to the ferro-quadrupole ordering. The critical slowing down of the relaxation time $\tau_0$ by the ultrasonic attenuation coefficient $\alpha_{66}$ and the large softening of the elastic constant $C_{66}$ are well described in terms of the divergence of the quadrupole susceptibility. The quenching of the quadrupole $O_{\chi',\gamma'}$ belonging to the $B_2$ irreducible representation of the tetragonal mother phase of the high-symmetry space group $D_{4h}$ brings about a distorted orthorhombic phase with the low-symmetry space group $D_{2d}$.\(^{17}\)

The rotation $\omega_{xy}$ of the transverse ultrasonic waves or transverse acoustic phonons twists the electronic states with angular momentum $l$. The rotation operator of $\exp[-i\omega_{xy}]$ acting on the Hamiltonian $H$ leads to the perturbation of $H_{\text{eff}}(\omega_{xy}) = i[l, H] \omega_{xy} = \tau_{xy} \omega_{xy}$, where the torque $\tau_{xy}$ is described by the Heisenberg equation $\dot{H}_{\text{eff}}/\dot{\theta} = [l, H] = i \tau_{xy}$. For the CEF Hamiltonian of $H = H_{\text{CEF}}$, the torque $\tau_{xy}$ corresponding to the hexadecapole of one-electron states, however, vanishes because of the rotational invariance for states in the central force in the absence of an external magnetic field.

The rotation operation on the anisotropic quadrupole interaction Hamiltonian consisting of $O_{\chi',\gamma'}$ and $O_{\chi',\chi'}$ gives the interaction of the hexadecapole $H_{\text{H}}^2(r, r') = O_{\chi',\gamma'}(r)O_{\chi',\gamma'}(r') + O_{\chi',\chi'}(r)O_{\chi',\chi'}(r')$ to the rotation $\omega_{xy}$ of the transverse ultrasonic waves. The critical slowing down of the relaxation time $\tau_\text{B}$ around the superconducting transition is well described in terms of the divergence of the hexadecapole susceptibility. This result indicates that the ferro-type hexadecapole ordering is caused by the quenching of the two-electron state belonging to the $A_2$ irreducible representation of the tetragonal phase with space group $D_{4h}$.\(^{17}\)

Supposing that the quadrupole interaction of $O_{\chi',\gamma'}$ mediated by the strain $\varepsilon_{ij}(q)$ of the transverse acoustic phonons with a small wavenumber favors the attractive force for pairs of electrons, we solve the superconducting Hamiltonian based on the anisotropic quadrupole interaction. The superconducting ground state consisting of two different energy gaps for the Cooper pairs possesses the energy dependence of $\cos[\varphi_{1+1}(k) - \varphi_{-1-1}(k)]$ for the phase difference of $\varphi_{1+1}(k) - \varphi_{-1-1}(k)$ between the two energy gaps. The Cooper pair bearing the hexadecapole proportional to $\sin[\varphi_{1+1}(k) - \varphi_{-1-1}(k)]$ couples to the rotation of $\omega_{xy}(q)$ of the transverse acoustic phonon. The hexadecapole interaction mediated by the rotation $\omega_{xy}(q)$ with the small-wavenumber limit of $|q| \to 0$ causes the ferro-type hexadecapole ordering in the superconducting phase, which brings about the spontaneous rotation $\omega_{xy}(0) \neq 0$ of the macroscopic superconducting state with respect to the host tetragonal lattice. This is in good agreement with the ground scenario that the critical slowing down around the superconducting transition is caused by the hexadecapole ordering. The simultaneous symmetry breaking of the U(1) gauge for the off-diagonal long-range ordering of the Cooper pairs and the freezing of the $A_2$ symmetry of space group $D_{4h}$ for the ferro-type hexadecapole ordering specify the unconventional superconductivity of the present iron pnictide.

The present experiments on the iron pnictide Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ showed that ultrasonic measurements by transverse ultrasonic waves carrying rotation as well as strain are a powerful means of detecting the hexadecapole and quadrupole effects of quantum systems with orbital degrees of freedom. We hope that the measurements of the hexadecapole as well as the quadrupole by the transverse ultrasonic waves will lead to the discovery of various exotic phenomena associated with magnetic and quadrupole orderings and unconventional superconductivity in strongly correlated electron physics.

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