Electronic and Superconducting Properties of the AFeAs (A = Li, Na) Family Alkali-Metal Pnictides: Current Stage of the Research (Brief Review)

T. E. Kuzmicheva* and S. A. Kuzmichev
Lebedev Physical Institute, Russian Academy of Sciences, Moscow, 119991 Russia
Faculty of Physics, Moscow State University, Moscow, 119991 Russia
*e-mail: kuzmichevate@lebedev.ru

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The review is focused on one of the most exotic families of iron-based superconductors belonging to the AFeAs structural class, where A is an alkali metal. We briefly concern physical and electronic properties of the typical members of this family, LiFeAs and NaFeAs, discuss the theoretical models describing the multigap superconducting state, and the experimental data available in literature. As well, we specify the main unsolved problems, that seem crucial for both, the AFeAs family and for iron-based superconductors in general.

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1. INTRODUCTION

Layered alkali-metal iron pnictides AFeAs, where A is an alkali metal, have moderate critical temperatures $T_c$ up to 22 K and belong to the so-called 111 structural family. Similarly to other iron-pnictide families, the crystal structure of the 111 family contains superconducting FeAs blocks separated by alkali metal blocks along the c direction. The 111 family members are not so numerous: stable chemical structures are formed only with alkali metals having small atomic radius (Li and Na), whereas the possible substitutions are limited by a certain set of transition metals TM = Co, Ni, Cu, V, Rh, or alkali metal deficiency A$_{1-x}$FeAs. Nonetheless, the AFeAs compounds show extraordinary properties that are not typical for the majority of the iron-based high temperature superconductors (HTSC) and strongly depend on the chemical composition. Accordingly, AFeAs pnictides are of great fundamental interest.

Using “self-flux” technique, it is possible to grow high-quality AFeAs single crystals (as large as 1 cm in dimension) [1–3]. However, experimentalists usually have to overcome a number of troubles when probing the properties of these peculiar compounds. For example, when exposing LiFeAs crystal in open air, its critical temperature decreases rapidly, dropping to zero in about 10–20 min, whereas LiOH emerges between FeAs blocks. Since the 111 family crystals are naturally cleaved along the blocks of active alkali metal atoms, their surface degrades inevitably, in presence of even trace amounts of oxygen or water vapors. Being exposed for a long time, nitrogen also reacts chemically with AFeAs. Although the bulk properties remain almost stable and insensitive to nitrogen, its presence appears fatal for the sample surface. Therefore, all preparations and the experiment have to be made in a “dry” vacuum or in a protective atmosphere.

Due to high quality of the cryogenic clefs provided that the experiment is carried out correctly, availability of large single crystals, and an absence of surface bands [4], the alkali-metal superconductors seem to be the best candidates for angle-resolved photoemission spectroscopy (ARPES) probes in order to determine the band structure features in a high resolution. Nonetheless, the above mentioned experimental troubles lead to the lack of experimental data on the properties of the 111 compounds measured by other techniques. In particular, the studies of the main characteristics of the superconductor, i.e., superconducting order parameter, its temperature dependence and symmetry, are rather scarce to date.

2. PHASE DIAGRAM

The phase diagram for the alkali-metal pnictides strongly differs from that for the majority of other iron based superconductors. It is widely known that relatively well studied REOF$_{2}$As oxypnictides of the 1111 family (RE is a rare-earth metal), as well as the 122 family pnictides AEF$_{2}$As$_{2}$ (AE is an alkali-earth metal) being in the stoichiometric state, at temperatures about $T_s$ ~ 120–150 K undergo a structural tran-
transition from the tetragonal phase ($T > T_s$) to the orthorhombic phase. At lower temperatures $T_m < T_s$, the structural transition is accompanied with antiferromagnetic transition to a spin density wave (SDW) state ($T < T_m$), the so-called nematic phase emerges in the RE-1111 and AE-122 family compounds being a nonmagnetic state with broken rotational symmetry in the crystallographic $ab$-planes ($a \neq b$). Superconducting phase showing a "dome" of the critical temperature develops in the tetragonal phase along with SDW and nematicity suppression under pressure or doping. On the contrary, superconductivity emerges in the stoichiometric state in the 111 family alkali-metal pnictides [3, 7–12]. Nonetheless, phase diagram of the 111 family is not universal and changes drastically for the compounds with various alkali metals.

LiFeAs compound is fully nonmagnetic [13] and naturally has optimal superconducting properties, with maximum critical temperature $T_c = 17–18$ K. As shown in [3, 9–11], superconductivity rapidly destroys under partial electron substitution (Fe,Co) within the superconducting FeAs blocks at $x \approx 0.12–0.16$ (Fig. 1). Similarly looking phase diagram was obtained for partial substitution by other transition metals (Ni, Cu, V) [14–16], as well as for LiFeAs under pressure [17], and for the crystals with lithium deficiency [18]. In the latter case, unfortunately, the dependence of $T_c$ on the deficiency $\delta$ for Li$_{1-x}$FeAs is not determined reliably to date. Long magnetic order establishes under neither any strong electron, nor any strong hole doping [9]. Noteworthy, such behavior resembles the evolution of magnesium diborides MgB$_2$ properties: superconducting properties of these nonmagnetic layered HTSC are also optimal in the stoichiometric state, whereas the critical temperature $T_c$ tends to zero under any available substitution (Mg,Al) or (B,C) [19]. However, the authors of recent work [20] reported signs of the coexistence of nematicity and superconductivity discussed below.

On the contrary, the orthorhombic phase and magnetic order develop in stoichiometric NaFeAs, although at much lower temperatures, $T_s \approx 55$ K and $T_m \approx 43$ K, respectively [3, 10–12], as compared to the 1111 and 122 family pnictides (Fig. 1). At $T_c \approx 10$ K, transport, magnetic, and calorimetric probes [3, 10, 11, 21, 22] show a superconducting transition as well. However, by contrast to LiFeAs, numerous studies [3, 7, 21, 22] show natural phase separation in NaFeAs: shunting superconducting clusters related to the tetragonal phase (about 10% of the bulk of the crystal) neighbor with AFM clusters. In (Fe,Co)-doped NaFeAs crystals, the structural and AFM transitions shift toward lower temperatures, with it, the volume of the superconducting fraction increases [12, 21]. Under cobalt doping, maximum $T_c \approx 22$ K is reached in the bulk tetragonal phase as the AFM and nematicity become suppressed, as shown in Fig. 1. Qualitatively similar phase diagram was obtained in [12] for NaFe$_{1-x}$Cu$_x$As substitution, but there superconductivity vanished much more rapidly with doping (yet for $x = 0.05$), whereas the maximum $T_c$ was as low as 12 K.
A presence of nematic fluctuations in LiFeAs and NaFeAs at $T > T_c$ was demonstrated in transport and NMR studies [7, 23].

3. BAND STRUCTURE AND THE FERMI SURFACES

For the majority of iron-based HTSC, hole barrels near the $\Gamma$-point and electron barrels near the M-point of the first Brillouin zone are formed at the Fermi level, both slightly warped along the $k_z$ direction of the momentum space, and connected by the nesting vector $\mathbf{Q} = (\pi, \pi)$ in the 2-Fe unit cell (for a review, see [5, 6, 24, 25]). Band structure calculations for the 111 family pnictides are presented in [26–28]. ARPES-studies [4, 9, 13, 14, 20, 26, 29–36] showed that the Fermi surfaces of the 111 pnictides hardly resemble those for other families, but show quite differences.

In stoichiometric LiFeAs, the radii of the Fermi surface barrels are strongly different (Fig. 2a): at the $\Gamma$-point, a shallow barrel is resolved, whereas the radius of the outer hole barrel is much larger than that of the electron barrels. As a result, nesting at the vector $\mathbf{Q} = (\pi, \pi)$ is fully absent in LiFeAs [9, 13–15]. Under electron substitution (Fe, Co), as shown in Fig. 2 taken from ARPES studies [9], the volume of the M-point barrels increases as the volume of the outer hole barrel diminishes. Just for the compound with $x = 0.12$ cobalt concentration, the Fermi surface barrels become fully nested (Figs. 2c, 2h). For hole-doped LiFe$_{1-x}$V$_x$As, as reported in [14], with $x$ decrease, only the inner $\Gamma$-point barrel expands (Fig. 3), thus becoming nested with the electron barrels at $x \approx 0.084$ (Fig. 3d).

It is interesting to account that in both cases, as shown in [9, 14], along with nesting in the $\Gamma$–M direction development, superconductivity becomes suppressed: an ideal nesting is reached in strongly overdoped Co-substituted LiFe$_{0.88}$Co$_{0.12}$As compound with $T_c \rightarrow 0$ (see the phase diagram in Fig. 1), and in nonsuperconducting LiFe$_{0.916}$V$_{0.084}$As compound (the (Li, V) doping phase diagram is shown in Fig. 1d in [14]). On the other hand, the data obtained in [15] question the universality of such statement: under (Fe, Cu) substitution, no significant Fermi surface reconstruction was observed. Then, such (Fe, Cu) substitution is actually isovalent, which is caused by the localization of the doping electrons, accordingly to the authors’ of [15] interpretation. Therefore, in order to reveal any correlation between the nesting quality and the $T_c$ value, further studies of the Fermi surface topology in doped LiFeAs seem of high importance.

Rather interesting results were obtained in recent high-resolution ARPES studies [26, 31]. In LiFeAs, as well as in iron-based HTSC of other families, a noticeable (about 10 meV) band splitting in the high symmetry points was detected, caused by the spin–orbit coupling (SOC) [26, 31]. In particular, the authors claim that namely SOC is responsible for the shallow Fermi surface barrel emergence near the $\Gamma$ point.

The features of the NaFeAs phase diagram provide an unique opportunity to observe the change in the symmetry of the crystal and band structure with temperature and doping using ARPES. However, from the experimental point of view, an intermediate problem arises. Generally, the formation of mirror-oriented crystallographic domains (twinning) is typical for single crystals of iron-based superconductors. Since the dimension of the domains is comparable with the ARPES beam diameter, the resulting experimental data is the superposition of the dispersion curves for the both domain orientations, thus making it impossible to resolve an in-plane anisotropy. Several detwining procedures are reviewed in detail in [37], in particular, a most widely used uniaxial deformation along $a$ and $b$ lattice directions.

Temperature evolution of the stoichiometric NaFeAs Fermi surface is shown in [36, 38] (Figs. 4a–4h). In the metallic phase with four-fold $C_4$ symmetry, the Fermi surface cross section at $k_z = 0$ represents a circle around the $\Gamma$-point, and two crossing ellipses in the corner of the Brillouin zone (see red profiles in Fig. 4a). The picture remain almost the same under applied uniaxial stress, as shown in (b). There, the nesting condition is satisfied only for several Fermi surface points, along $k_x$ and $k_y$ directions. With temperature decrease, the $C_4$ symmetry breaks: in the nematic phase, hole barrel distortion along the stress direction, and disappearance of one of the ellipses around the M point are well visible (Figs. 4c–4e). Finally, in the AFM phase, the most of the Fermi surface pockets are gapped (Figs. 4g, 4h).

In superconducting Na(Fe,TM)As, contrary to LiFe(Fe,TM)As, doping does not lead to full nesting between electron and hole pockets at $k_z = 0$ [32–35], although the possibility of quite ideal nesting for several $k_z$ values was supposed in [32].

A minor distortion (about 4%) of the outer hole barrel at the center of the Brillouin zone was resolved in very recent ARPES probe [20] of twinned stoichiometric LiFeAs below $T_c$ (Figs. 4i, 4j). The reasons facilitating the observation of the $ab$–plane anisotropy without uniaxial stress applied are discussed by the authors. Anyway, such $C_4$ symmetry breaking below $T_c$ could indicate superconductivity development in the nematic phase, that was not observed earlier in any high-temperature superconductor excepting FeSe. Moreover, since the asymmetry of the band structure resolved at low temperatures vanishes above $T_c$, the authors of [20] suppose superconductivity responsible for the observed nematicity in LiFeAs.
One of the earlier theoretical works [39] shows that despite observation of partial isotope effect [40], electron–phonon coupling appears rather weak in the iron-based superconductors, thus being insufficient to provide their relatively high $T_c$. Later, in order to describe the superconducting mechanism in the iron pnictides and chalcogenides, several theoretical models were suggested. In the framework of spin-fluctuation models, where the Cooper pairs are formed via the nesting between the Fermi surface parts of the same kind of orbitals (so-called “intraorbital” pair-
ing), it is possible to obtain a sign-reversal superconducting order parameter of $s^\pm$-type [41–45] (formally, negative superconducting gap $\Delta < 0$ for one Cooper pair condensate implies the phase of its wavefunction is shifted by $\pi$ as compared to that of another condensate), or complex $s + i\sigma$-type [46] (with arbitrary phase shift between superconducting condensates, different from $\pi$, and broken time reversal symmetry).

Spin resonance at the nesting vector $\mathbf{Q} = (\pi,\pi)$ was widely observed in the superconducting state in inelastic neutron scattering experiments with iron-based superconductors of various families (for a review, see [44, 47, 48]). Also it is worth noting that in some tunneling probes using break-junction technique [49–51] and point contact Andreev reflection (PCAR) technique [52, 53], the resonant interaction between Andreev current and a characteristic bosonic mode, possibly a spin exciton, was observed in the superconducting state: the boson energy at $T \ll T_c$ did not exceed an indirect superconducting gap $\Delta_2(0) + \Delta_3(0)$ or $2\Delta_1(0)$, thus satisfying the spin resonance condition in accordance with the calculations [54, 55].

On the other hand, coupling through nematic fluctuations [56] or orbital fluctuations enhanced by phonons [57–59], the strong intraband electron–phonon interaction [60], as well as accounting for Fano–Feshbach resonance near a Lifshitz transition or a BCS–BEC crossover [61] lead to the so-called $s^{++}$-symmetry of the superconducting order parameter without sign change (i.e., the wavefunctions of all the superconducting condensates are in phase). At once, spin fluctuations could be considered as an additional pairing channel responsible for a strong anisotropy of the superconducting order parameter, even sign-reversal [56, 58, 60].

Due to the Fermi surface features of LiFeAs [9, 13–15], in general, a pronounced spin resonance at the $(\pi,\pi)$ is hardly expected. Indeed, in the only work [62] a weak spin–resonance maximum was detected below $T_c$ at the energies $\varepsilon_0 = 6–11$ meV and at the vector $\mathbf{Q}$. The authors of [63] have also observed some resonance with energy $\varepsilon_0 = 5$ meV, however, do not speculate on its origin. On the other hand, theoretical calculations [45, 58, 59] predict a robust gap solution with $s^\pm$-symmetry even in case of poor nesting in the $\Gamma$–M direction, whereas the superconducting gap with the smallest absolute value supposed to develop at the smallest Fermi surface pocket. Accounting orbital selectivity (different correlation strengths in the bands formed by different orbitals; in particular, Cooper pairing strength) within the $s^\pm$-approach, the authors of [64] qualitatively reproduced the gap structures obtained in [45, 58, 59] for “pure” $s^\pm$-case, excepting that the condensate with the large superconducting gap developed at the inner hole barrel below $T_c$.

The existence of the bosonic mode in LiFeAs is under discussion now. Optical studies [65] have not reported any overgap features, those would be typical for the superconducting state below $T_c$. In the incoherent multiple Andreev reflections effect (IMARE) spectroscopy studies of LiFeAs single crystals, a fine structure caused by resonant coupling with a bosonic

![Fig. 3. (Color online) Fermi surface evolution with hole doping for LiFe$_{1-x}$V$_x$As single crystals with various vanadium concentrations as determined by ARPES. Red dashed lines depict the Fermi surface profiles for stoichiometric LiFeAs (the same as shown by solid red lines in panel (a)). Solid lines in panels (b–d) illustrate the profiles of the inner hole barrel for the labelled concentrations $x$. The figure is taken from [14] with the authors’ and publisher’s permission. © (2021) American Physical Society.](image-url)
mode was reproducibly absent [66, 67], although it was well-resolved in the 1111 oxypnictides of various composition [49–51]. In the scanning tunneling microscopy (STM) probes [68–70], an overgap dip–hump structure appeared in the obtained \(dI/dV\)-spectra was interpreted within the approach [68, 70] as a footprint of the electron density of states (DOS) renormalization caused by a spin resonance. On the other hand, in the works [71–73] a set of arguments against such interpretation was suggested. In particular, the authors of [72] attribute the dip–hump structure to a coupling with nematic fluctuations, whereas the authors of [73] show that similar dip–hump structures usually appear in the \(dI/dV\)-spectra of tunneling junctions owing to surface defects influence. Theoretical calculations [58, 59] showed that a moderate anisotropy (including that along the \(k_z\)-direction) of the superconducting gaps developing below \(T_c\) at electron and hole barrels could be obtained even accounting \(s^{++}\)-interaction between the Fermi surface parts formed by different orbitals solely (so-called “interorbital” coupling). Moreover, when combining the pairing channels via spin and orbital fluctuations, it is possible to simulate almost any kind of gap anisotropy, even nodal (turning to zero at certain momenta \(\Delta(k) = 0\) or sign-reversal. The most important results of these studies [58, 59] are: (a) the largest superconducting gap developing at the smallest Fermi surface pocket (the inner barrel around the \(\Gamma\)-point) at the strong \(s^{++}\)-interaction limit; (b) if the strengths of the
$s^{++}$ and $s^{\pm}$-interactions are comparable, the "negative" superconducting order parameter develops only at the outer hole barrel, whereas $|\Delta| \to 0$ for this band.

Multiple-gap superconducting state of NaFeAs could be described in the both frameworks, a universal $s^{\pm}$-approach [74], and accounting orbital selectivity [75]. An observation of a weak spin resonance with energy $e_0/(k_B T_c) = 4-6$ in underdoped and optimally doped Na(Fe,TM)As (TM = Co, Cu) below $T_c$ was reported in [12, 76–79]. In overdoped NaFe$_{0.92}$Co$_{0.08}$As, according to [78], despite the significantly lower $T_{c_{0}}$ at the outer hole barrel, whereas for this band.

Figure 5 shows the dependence of the characteristic ratios $2\Delta_i(0)/(k_B T_c) \equiv r^B_{BCS}$ on the critical temperature basing on the data obtained in literature. The critical temperatures $T_c < 18$ K obtained in the most of papers for the single crystals of nominal LiFeAs composition seems very likely caused by a local lithium deficiency, hence, hereafter we will use the Li$_{1-\delta}$FeAs notation.

ARPES experiments [20, 29, 30] revealed a presence of at least three superconducting condensates. Despite the absolute values $\Delta_i(0)$ are little contradictory (circles in Fig. 5, right panel), the data are qualitatively similar: at $T < T_c$ the largest superconducting gap develops at the inner hole barrel, whereas the smallest gap develops at the outer one. Additionally, the order parameters have a valuable anisotropy in the momentum space. Such gap structure agrees well with the calculations [58, 59] within the $s^{++}$-approach (without sign change), as well as could be reproduced in the framework of $s^{\pm}$-model accounting orbital selectivity [64] (for a sign-reversal order parameter).

In the electron bands [20, 30] superconducting order parameters have middle, almost similar magnitudes. Although in earlier studies [29, 30] four-fold (90° rotation symmetry) angle dependences of the gaps $\Delta_i(\theta)$ were supposed (where $\theta$ is the angle in the $k_xk_y$-plane), very recent high-resolution probes [20] showed that $\Delta_i(\theta)$ could be well fitted by a two-fold function (180° rotation symmetry). The latter corroborates the authors’ claim [20] about the superconductivity development in the nematic phase.

The data obtained by tunneling [67–72, 84, 85], bulk [86–90], and surface probes [65, 91] summarized on the left panel of Fig. 5 are obviously grouped into three bunches with the characteristic ratio ranges 0.9–2.4, 3.1–5.1, and 7.2–10.3. Hereafter, the superconducting order parameters are denoted as $\Delta_1$, $\Delta_2$, and $\Delta_3$, respectively. Using IMARE spectroscopy [67], three distinct superconducting order parameters were directly measured (stars in Fig. 5): the small gap with the characteristic ratio $r^B_{BCS} = 1.7 \ll 3.53$ showing no signs of anisotropy, rather strongly anisotropic middle gap with $r^B_{BCS} = 3–5$, and minor split large gap with $r^B_{BCS} = 7.3–8.4$ (the value ranges correspond to the anisotropy degree, about 40 and 14%, respectively). Aside from the above mentioned data, an anisotropy of the superconducting order parameters was resolved only in [84] by quasiparticle interference technique (connected triangles in Fig. 5): clearly, this data agrees well with the IMARE results [67] in both, the anisotropy degrees of the large and the middle gaps, and in the values of their characteristic ratios.
We note that in STM experiments [68–72, 84, 85], only two superconducting gaps are observed, the large and the middle ones (triangles in Fig. 5). For the large gap, the values estimated in [68, 69, 85] correspond to the anisotropy range determined in [67, 84]. The characteristic ratio of the order parameter developing at the inner hole barrel estimated in [30] lays within this range as well, whereas similar data from [20, 29] appear a bit lower. At the same time, another STM probes [70–72] report higher characteristic ratio values, up to 10.3. One could suppose, since the superconducting gap magnitudes in [70–72] were estimated directly from the positions of the tunneling maxima in the $dI/dV$-spectra, an influence of inelastic processes characterized by the broadening parameter $\Gamma = \hbar/2\tau$ (where $\tau$ is the characteristic energy relaxation time), is a reason of such gap overestimation. A finite $\Gamma$ value generally leads to both, the broadening of the electron DOS peaks and the gap-edge shifting toward higher energies. According to recent ARPES studies [92], in LiFeAs the $\Gamma$ value could be extremely high, even comparable with $\Delta(0)$.

Temperature dependences of the superconducting gaps in Li$_{1-\delta}$FeAs are obtained using only two experimental methods to date. The dependences of the three gaps $\Delta_{1,2,3}(T)$ directly determined using IMARE spectroscopy are typical for the case of a moderate interband coupling, whereas the anisotropy degrees of the $\Delta_{2,3}$ remain almost constant within a wide temperature range [67]. Similarly looking temperature behavior of the large and the middle gaps $\Delta_{2,3}(T)$ was obtained in [69] using fitting with the Dynes model of the $dI/dV$-spectra measured at $T < T_c$.

On the other hand, bulk studies (measurements of the specific heat and the lower critical field) [86–89] as well as surface studies (infrared (IR) reflection spectroscopy, surface impedance measurements) [65, 91] report an observation of the middle and the small gap (squares and rhombs in Fig. 5). Possibly, it relates with a low Cooper pair concentration in the condensate with the large gap, as shown in [67]. Nonetheless, the observed data diversity for the $T_c \approx 16.5$ K represent the characteristic ratios averaged over those determined by the authors in the IMARE studies of ten Andreev junctions with the corresponding local critical temperature obtained in LiFeAs single crystals.
middle gap (cyan symbols in Fig. 5) matches exactly its anisotropy range determined in [67, 84], and also agrees with the characteristic ratio ranges for the anisotropic order parameters in the electron band estimated using ARPES [29, 30]. As well, one should not exclude a possible anisotropy of the small gap (accounting that in ARPES probes, pairing anisotropy was observed for all the bands, see connected circles in Fig. 5, right panel) as a reason of the scattering of its characteristic ratio 1.0–2.5 (black symbols in Fig. 5). However, ARPES estimates provide a bit higher values.

Fig. 6. (Color online) Experimental dependence of the characteristic ratios of the superconducting gaps $2\Delta_i(0)/(k_B T_c)$ determined using STM (triangles) [94, 95], specific heat probes (squares) [12, 10], and ARPES (circles) [32, 33, 93] versus critical temperature $T_c$ in doped Na(Fe, Co)As. The circles are colored corresponding to the electron and hole Fermi surface pockets sketched. The connected symbols illustrate the anisotropy degree of the large superconducting order parameter. Dashed areas cover the ranges of the obtained values of the superconducting gap characteristic ratios. For comparison, the dependences of the characteristic ratio of the spin resonance energy $\epsilon_s/(k_B T_c)$ versus $T_c$ are presented (solid stars for the high-energy mode, open stars for the low-energy one), as determined in inelastic neutron scattering studies [76–78]. Dash-dotted line shows the weak-coupling BCS limit.

Specific heat measurements of Na(Fe, Co)As samples with various doping degree [10, 12] (squares in Fig. 6) showed a presence of the large superconducting gap with $2\Delta_i(0)/(k_B T_c) \approx 6.3–7.5$ well-exceeding the weak-coupling BCS limit, as well as the small gap with the characteristic ratio 2.6–3.6. With it, similar data [12] obtained for underdoped sample from the same batch with $T_c \approx 12.3$ K were well fitted with a single-gap model.

The authors of the ARPES studies of Na(Fe, Co)As [32, 33, 93] agree that a uniform superconducting condensate develops at two electron barrels of the Fermi surface. Nonetheless, the exact values of the energy parameters are rather contradictory (circles in Fig. 6). The two studies of overdoped crystals [33, 93] reported that the superconducting gaps developed in the electron and the hole bands are quite similar, but the corresponding characteristic ratios determined in [33, 93] are rather different (green and orange symbols in Fig. 6, right panel): the lowest value $r_{i^{BCS}} = 4$ [32] agrees well with that of the small gap estimated using a specific heat temperature dependence [12, 45].
whereas the highest values $r_C^{\text{BCS}} \approx 5.8–8.8$ [33, 93] lays within the range for the large gap determined using STM [10, 12, 94, 95]. For an underdoped composition (left panel of Fig. 6), a strong anisotropy of the large order parameter developing at the electron pockets was resolved using ARPES [93], but was not been observed by the same group for an overdoped crystal with similar $T_c$. An appearance of the superconducting order parameter anisotropy within the region where AFM and superconducting phases naturally coexist, may indicate a possible SDW influence to the gap structure, thus needing in further detailed studies with high energy resolution.

Among the other groups, the phenomenon of superconducting gap anisotropy is being discussed now. The specific heat data $C_e(T)$ [10, 12] and thermal conductivity measurements [96] are well fitted with (nodeless) isotropic order parameters. On the other hand, the authors of [12] do not exclude an anisotropy of the superconducting properties, if accounting the limitations of the model used to fit the $C_e(T)$ data with. At the same time, the temperature dependence of the Cooper pair concentration (determined using the London penetration depth measurements) is claimed [97] to be fitted in the framework of anisotropic superconducting gaps for both, underdoped and overdoped compositions. Contrary, the tunneling spectra obtained in [95] could be fitted with the Dynes model for both, isotropic and anisotropic gap, by varying the broadening parameter $\Gamma$. Unfortunately, the tunneling data for Na-111 are almost absent: the available probes made by STM [94, 95] have resolved only a single superconducting gap, whereas Andreev spectroscopy experiments have not been made at all.

In order to compare with the gap parameters, the characteristic ratios of the spin resonance energy $\varepsilon_0/(k_BT_c)$ are also shown in Fig. 6 (stars), those determined in inelastic neutron scattering studies of Na(Fe,Co)As [76–78]. As mentioned above, the double spin resonance is reproducibly observed in underdoped region [76–78] (left panel of Fig. 6): the energy of the first resonance mode $\varepsilon_0^{\text{min}}$ (low-energy mode existing in the AFM phase at $T < T_{\text{m}}$) keeps almost independent with $T_c$, thus resulting in the increase in its characteristic ratio when approaching the AFM phase (open stars in Fig. 6). For the second resonance (observed in the superconducting state only), the value $\varepsilon_0^{\text{max}}/(k_BT_c) = 4.2–4.9$ weakly depends on doping (solid stars in Fig. 6), excepting a single dropped out point on the right. In Na(Fe, Cu)As crystals with slightly overdoped composition and $T_c \approx 12$ K, a bit higher ratio $\varepsilon_0/(k_BT_c) \approx 5.5$ was obtained in [12]. Note-worthily, the $\varepsilon_0^{\text{max}}/(k_BT_c)$ data shown in Fig. 6 are located almost in the middle between the characteristic ratios for the large and the small gaps; more precisely, $\varepsilon_0^{\text{max}} = 2.5\Delta^*(0)$ being less than $\Delta_L^*(0) + \Delta_S^*(0)$. Therefore, in accordance with the available data statistics shown in Fig. 6, the spin resonance condition predicted theoretically in [54, 55] is satisfied in Na(Fe, Co)As.

### 6. CONCLUSIONS

The above brief review shows that the studies of the alkali-metal-based superconductors of the 111 family, discovered about 13 years ago, are far from being finished yet. The available experimental data are rather contradictory and mostly inconsecutive. Nonetheless, due to their extraordinary properties that are not typical for other families of iron-based superconductors, namely, the A-111 family pnictides could be crucial for answering the majority of fundamental questions. The most important experimental problems seem as follows:

—A direct measurement of the structure of the superconducting order parameter (the number, magnitudes, symmetries, and the characteristic ratios of the superconducting gaps, their temperature dependences, and a possible phase shift $s + is$) in doped $\text{AFe}_1-x\text{TM}_x\text{As}$ ($\text{A} = \text{Li, Na}; \text{TM} = \text{Co, Ni, Cu, V, Rh}$), as well as in the compounds with alkali metal deficiency $\text{A}_{1-\delta}\text{Fe}_x\text{As}$, with various $x$ and $\delta$. A comparison between the properties of underdoped and overdoped crystals with electron, hole, and isovalent substitution, and revealing the evolution of their properties along the corresponding doping phase diagrams.

—Inelastic neutron scattering studies of the so-called spin resonance phenomenon (the determination of the energy $\varepsilon_0$, its characteristic ratio to $k_BT_c$, and temperature dependence) in overdoped Na(Fe, Co)As, as well as in Na-111 pnictides with iron substitution for other transition metals (Cu, Rh, etc.) or with Na deficiency within the whole doping range available. The uncovering of the nature of the bosonic mode, its energy, and temperature dependence using high-resolution tunneling probes.

—A further detailed study of a possible coexistence between nematicity and superconductivity in LiFeAs, as well as in other iron-based superconductors.

An experimental verification of the above mentioned issues seems to define, to what extent the features of the band structure, magnetism and nematicity influence the superconducting subsystem. Without any doubts, the solving of the listed problems would facilitate an adaptation and generalization of the theoretical models in order to describe the physics of iron pnictides and chalcogenides. Hopefully, this will bring the researchers to the answer the central question: whether the mechanism of unconventional superconductivity is universal for different families of pnictides and chalcogenides?
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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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