#### **REVIEWS OF TOPICAL PROBLEMS**

PACS numbers: 74.20. - z, 74.25. - q, 74.62. - c, 74.70. - b

### FeAs systems: a new class of high-temperature superconductors

Yu A Izyumov, E Z Kurmaev

**Contents** 

DOI: 10.1070/PU2008v051n12ABEH006733

1.	Introduction	1261
2.	Compounds of the <i>RE</i> OFeAs type	1262
	2.1 Crystal chemistry and the basic physical properties of doped compounds; 2.2 Magnetic properties; 2.3 Electronic	
	structure; 2.4 Symmetry of the superconducting order parameter	
3.	Compounds of the $AFe_2As_2$ type ( $A = Ba, Sr, Ca$ )	1270
	3.1 Electronic structure; 3.2 Superconducting order parameter; 3.3 Doping and pressure; 3.4 Magnetism	
4.	Compounds of the LiFeAs and FeSe types	1276
	4.1 Electronic structure and superconductivity in LiFeAs; 4.2 Superconductivity in FeSe-type compounds	
5.	Theoretical models	1277
	5.1 Theoretical problems; 5.2 The minimal two-band model; 5.3 The s <sup>+</sup> symmetry of the order parameter;	
	5.4 Derivation of the effective Hamiltonian; 5.5 Role of electron correlations	
6.	Conclusion	1284
	References	1285

Abstract. This is the first systematic review of a new class of high- $T_{\rm c}$  superconductors that includes iron-based layered compounds such as REOFeAs (RE is a rare-earth element),  $AFe_2As_2$  (A = Ba, Sr, Ca), and LiFeAs, all of which are antiferromagnetic normal metals while being stoichiometric and becoming superconducting (with the current maximum  $T_{\rm c}$ given by 55 K) when doped with an element of a different valence. The common structural element of all these compounds is layers formed by FeAs<sub>4</sub> complexes. Electron states near the Fermi level are formed by Fe 3d states. As was shown theoretically by LDA calculations and experimentally by ARPES, the electronic structure of all compounds of the FeAs class is similar; their Fermi surface is multi-sheeted, consisting of two hole pockets at the center and two electron pockets at the corners of the Brillouin zone. In this paper, the superconducting properties of such systems are reviewed in detail, including the dependence of  $T_{\rm c}$  on the doping level, external pressure, superconducting critical field, and superconducting order parameter. The controversy over the order parameter symmetry determined from different measurements is discussed. The transport, magnetic, and superconducting properties of FeAs systems are analyzed in comparison with those of cuprates. Basic electronic models of FeAs compounds, with their electronic structure and the proximity of the state of doped compounds

Yu A Izyumov, E Z Kurmaev Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, ul. S. Kovalevskoi 18, 620219 Ekaterinburg, Russian Federation Tel. (7-343) 374 41 93, (7-343) 374 41 83. Fax (7-343) 374 52 44 E-mail: yuri.izyumov@imp.uran.ru, kurmaev@ifmlrs.uran.ru

Received 1 September 2008 Uspekhi Fizicheskikh Nauk **178** (12) 1307–1334 (2008) DOI: 10.3367/UFNr.0178.200812d.1307 Translated by S N Gorin; edited by A M Semikhatov to the antiferromagnetic ordering taken into account, are described to explain the specific features of electron pairing in them. It is shown that unlike the cuprates, superconducting FeAs systems are weakly (or moderately) correlated materials that are far from the Mott – Hubbard transition. A conclusion is made that the physical properties of FeAs compounds have mainly been well understood, except for the symmetry of the superconducting order parameter.

#### 1. Introduction

The first communication on the superconductivity of LaOFeAs [1] appeared as early as 2006, but the temperature  $T_c$  of the superconducting transition proved to be low,  $T_c = 3.5$  K. Similarly, for LaONiP,  $T_c = 4.5$  K was obtained [2]. A breakthrough occurred in February 2008, when Kamihara revealed superconductivity at  $T_c = 26$  K in the fluorine-doped compound LaO<sub>1-x</sub>F<sub>x</sub>FeAs [3]. Later, by substituting other rare-earth elements for La, several Chinese groups obtained considerably higher values ( $T_c = 41$  K in CeO<sub>1-x</sub>F<sub>x</sub>FeAs [4],  $T_c = 52$  K in PrO<sub>1-x</sub>F<sub>x</sub>FeAs [5]) and reached  $T_c = 55$  K in SmO<sub>1-x</sub>F<sub>x</sub>FeAs [6].

The initial undoped compounds are antiferromagnetic (AFM) metals, in which magnetic ordering appears at the Néel temperature  $T_N \approx 140$  K (in LaOFeAs), along with the structural phase transition from the tetragonal to the orthorhombic phase. As oxygen is replaced with fluorine,  $T_N$  decreases sharply with increasing the concentration of F, and at  $x \simeq 0.1$ , the long-range magnetic order disappears and a superconducting state occurs. A phase diagram on the plane (T, x) typical of the compounds of this type is shown in Fig. 1 [7].

This diagram resembles the diagrams characteristic of the cuprate-type high-temperature superconductors (HTSCs), e.g.,  $(La_{1-x}Sr_x)_2CuO_4$ . In cuprates, the superconductivity appears in compounds of the La<sub>2</sub>CuO<sub>4</sub> type (which are also



**Figure 1.** Typical phase diagram of  $REO_{1-x}F_x$ FeAs compounds (*RE* is a rare-earth element) on the (T, x) plane.  $T_s$  is the superconducting transition temperature [7].

AFM while being stoichiometric) as lanthanum is replaced by strontium. In both systems, the doping introduces charge carriers (electrons or holes), which suppresses the AFM ordering and creates conditions for Cooper pairing. This analogy has led to the assumption that the high-temperature superconductivity of the new FeAs-type superconductors is caused by the proximity of the system to the magnetic phase transition; in this case, high values of  $T_c$  are caused by the pairing of charge carriers through spin fluctuations.

The analogy between FeAs systems and cuprates becomes even closer when we compare their crystal structures. FeAs systems are built of alternating FeAs planes separated by LaO planes, similarly to how the alternating  $CuO_2$  planes are separated by LaBa or YBa planes in cuprates. Systems of both types are strongly anisotropic because of their layered structure, and the electron states in them are quasi-twodimensional.

Soon after the *RE*OFeAs compounds (where *RE* is a rareearth element), compounds of the *A*Fe<sub>2</sub>As<sub>2</sub> type (A = Ba, Sr, Ca) were discovered, in which pairs of FeAs planes (bilayers), similar to the bilayers in cuprates of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> type, alternate. In doped *A*Fe<sub>2</sub>As<sub>2</sub> compounds, superconductivity at  $T_c = 38$  K was revealed immediately [8]. Then, one more class of FeAs systems was discovered, namely, an LiFeAs compound, in which FeAs planes are separated by Li layers. It becomes superconductive at  $T_c = 18$  K, even without doping [9, 10].

An analogous property is characteristic of one more structural type, comprising FeSe, FeS, and FeTe, which are quite similar to compounds of the FeAs group. These new compounds are built from FeSe planes, in which, similarly to FeAs structures, square layers of Fe atoms, each surrounded by a tetrahedron of Se or Te atoms, alternate but are not separated by any other layers. In one such compound, FeSe, superconductivity at  $T_c = 27$  K was revealed at the pressure ~ 1.5 GPa [11].

Thus, we now have three classes of compounds built from FeAs planes (LaOFeAs,  $AFe_2As_2$ , and LiFeAs) and analogous compounds of the FeSe type, in which superconductivity with relatively high  $T_c$  is revealed. Their physical properties are similar in many respects, which can be related to the similarity of their crystal structure, because in all cases it involves a common element, the FeAs layers. This assumption is confirmed by many detailed physical studies.

The results of calculations of the electron-phonon coupling in these compounds showed [12, 13] that the high

values of  $T_c$  in these new compounds cannot be explained in terms of the standard electron – phonon pairing mechanism.

#### 2. Compounds of the *RE*OFeAs type

## 2.1 Crystal chemistry and the basic physical properties of doped compounds

The highest values of  $T_c$  have been obtained in a number of doped *RE*OFeAs compounds (Table 1). At room temperature, all these compounds have a tetragonal structure belonging to the space group *P4/nmm*. Their crystal structure is formed by alternating FeAs and LaO layers. An FeAs layer actually consists of three closely spaced atomic planes, which are arranged in a square lattice of Fe atoms, above and below which there are located square lattices of As atoms arranged relative to the Fe plane such that each Fe atom is surrounded by a tetrahedron of As atoms. In other words, an FeAs layer is formed by FeAs<sub>4</sub> complexes. The spacing between FeAs and LaO layers is 1.8 Å.

 Table 1. Maximum temperatures of the superconducting transition in doped *RE*OFeAs compounds.

RE	$T_{\rm c}, {\rm K}$	References	a, Å*	<i>b</i> , Å*		
Y	46.5	[14]				
La	41	[15]	4.035	8.740		
Ce	41	[4]	3.996	8.648		
Pr	52	[5]	3.925	8.595		
Nd	51.9	[16]	3.940	8.496		
Sm	55	[6]	3.940	8.496		
Gd	53.5	[17]				
Tb	48.5	[14]	3.898	8.404		
Dy	52.2	[14]				
Но	50.3	[14]				
* Lattice parameters of undoped compounds.						

The crystal structure of LaOFeAs is shown in Fig. 2a. The lattice parameters of *RE*OFeAs compounds are given in Table 1. It can be seen that the tetragonal unit cell has a rather elongated shape, which results in a strong anisotropy of all its properties and the quasi-two-dimensional nature of related electron states. The nearest neighbors of the Fe atoms are As atoms that separate the nearest adjacent Fe atoms, and hence the electron transfer over the iron sublattice is caused by Fe-As hybridization; in this case, the exchange interaction between Fe atoms occurs not directly but through As atoms.



Figure 2. Crystal structure of LaOFeAs and BaFe<sub>2</sub>As<sub>2</sub> compounds.

The crystallochemical properties of LaOFeAs compounds are determined by the configuration of the outermost electron shells of the atoms, i.e., Fe(4s4p3d), As(4s4p), La(6s5d4f), and O(2s2p). The valence of ions in the compound is expressed by the formula  $La^{3+}O^{2-}Fe^{2+}As^{3-}$ .

Upon substitution of F for O, the excess electron passes into the FeAs layer; this process is conventionally called the electron doping. When La is replaced, for example, by Sr, an electron vacancy is formed in the LaO layer, which is filled by an electron that passes from the FeAs layer, thus creating a hole in it. This process is called the hole doping. The redistribution of electrons between the LaO and FeAs layers upon doping results in the appearance of conductivity in the compound; the nature of charge carriers in it can be determined experimentally from the sign of the Hall constant  $R_{\rm H}$ .

Hall effect measurements were performed on the compound LaO<sub>0.9</sub> $F_{0.1}$ FeAs [18] with  $T_c = 24$  K soon after the superconductivity of this compound with  $T_c = 26$  K was discovered in [3]. It was found in [18] that  $R_{\rm H}$  is negative and only weakly depends on the temperature up to T = 240 K. This indicates that the conductivity is dominated by electrons. Based on the values of the Hall coefficient measured at  $T \approx 100$  K, the number of charge carriers was determined to be  $n \approx 9.8 \times 10^{20}$  cm<sup>-3</sup>. These results were confirmed in [19]. The measurements of  $R_{\rm H}$  on a sample of a slightly different composition (LaO<sub>0.89</sub>F<sub>0.11</sub>FeAs with  $T_c = 28.2$  K) at a temperature slightly exceeding  $T_c$  showed that the electron density in it is  $n \approx 1 \times 10^{21}$  cm<sup>-3</sup> [20], which virtually coincides with the density obtained in Refs [18, 19]. Compounds with other rare-earth elements, for example,  $NdO_{0.82}F_{0.18}FeAs$  [21], also show the electronic nature of charge carriers.

A remarkable fact was the discovery of HTSC in *RE*OFeAs compounds not doped with fluorine but having an oxygen deficit. High  $T_c$  values were reported in [22] for compounds such as LaO<sub>0.6</sub>FeAs ( $T_c = 28$  K), LaO<sub>0.75</sub>FeAs ( $T_c = 20$  K), and NdO<sub>0.6</sub>FeAs ( $T_c = 53$  K). The data for the *REO*<sub>1- $\delta$ </sub>FeAs compounds with *RE* = Sm, Nd, Pr, Ce, and La are given in Refs [4–6, 15–17]. The highest value of  $T_c$  for these compounds,  $T_c = 55$  K, was obtained in the SmO<sub>1- $\delta$ </sub>FeAs compound. Thus, doping with fluorine and the presence of oxygen vacancies exert the same effect on the initial stoichiometric compounds: the occurrence of electron-type carriers, suppression of the AFM ordering, and the appearance of a superconducting state.

We now consider the effects of substituting dopants with another valence for a rare-earth element. The substitution of a tetravalent element for a trivalent  $RE^{3+}$  element results in the electron doping. For example, in  $Gd_{1-x}Th_xOFeAs$ ,  $Th^{4+}$ substitutes for  $Gd^{3+}$ . At  $x \approx 0.1$ , this compound exhibits superconductivity with  $T_c = 55$  K [23].

A completely different situation arises upon substitution of a divalent element for an  $RE^{3+}$  ion. The substitution of  $Sr^{2+}$  for La<sup>3+</sup> in LaOFeAs results in the hole doping. At the Sr concentration x = 0.13, the La<sub>1-x</sub>Sr<sub>x</sub>OFeAs compound becomes a superconductor with  $T_c = 25$  K [24]. This is the first superconductor in the FeAs system obtained by hole doping, as follows from measurements of the Hall coefficient  $R_{\rm H}$ , which is positive in this compound [25]. It turned out that as the Sr concentration increases, the AFM order present in the initial compound is suppressed, as usual, and the doped compound already becomes superconducting at x = 0.03. The value of  $T_c$  increases with increasing x and reaches the value  $T_c = 25$  K at  $x \approx 0.11 - 0.13$ . With oxygen replaced by fluorine,  $T_c = 26$  K. We note that there is a kind of electronhole symmetry: upon doping the initial compound with electrons or holes,  $T_c$  increases in approximately the same way. But there is also some difference between these two types of doping. Upon doping with Sr, the increase in  $T_c$  is accompanied by a monotonic increase in the lattice parameters *a* and *c*, while upon doping with F, an increase in  $T_c$  is accompanied by a decrease in the lattice parameters [25].

These examples show that the superconductivity in FeAs systems can be initiated by either electron doping (substitution of fluorine for oxygen or creation of oxygen vacancies) or by hole doping (substitution of Sr for La). These tendencies are retained in all compounds of the *RE*OFeAs class.

It has been shown at the early stages of studying the *RE*OFeAs system that superconductivity appears when the dopants that replace oxygen or a rare-earth element are located outside the FeAs layers. Owing to the substitution of fluorine for oxygen or to the formation of oxygen vacancies in FeAs layers, there appear charge carriers, which suppress the antiferromagnetic order of a stoichiometric compound and lead to superconductivity. In this respect, the new superconductors are analogous to cuprates, in which the dopants replace the elements that are located outside  $CuO_2$  planes.

The substitution of Co atoms for Fe atoms located in FeAs planes also leads to the suppression of antiferromagnetism and the appearance of superconductivity already at small concentrations of the dopant. In this respect, the new superconductors strikingly differ from the cuprates, in which any interference in the CuO<sub>2</sub> planes suppresses superconductivity. In the simultaneously published works [26, 27], surprising results were obtained for different samples of the LaOFe<sub>1-x</sub>Co<sub>x</sub>As system. At x = 0.05, the suppression of antiferromagnetism was observed, while at  $x \approx 0.1$ , superconductivity appeared with  $T_{\rm c} \approx 10$  K and then disappeared at x > 0.15. According to the phase diagram of this system on the (T, x) plane [27], in the interval of the existence of the superconducting phase at  $T > T_c$ , a semiconductor conductivity is revealed, which is changed at  $T \approx 100$  K by the metallic conductivity. Analogous results were obtained for  $SmOFe_{1-x}Co_xAs$  [28].

Therefore, it turns out that Co is an efficient dopant for the induction of superconductivity. It is surprising that superconductivity is retained in a rather wide range of disorder (wide interval of x); this seems to be an argument in favor of the nonstandard symmetry of the order parameter, which is insensitive to magnetic impurities [29]. It is interesting to note that at x = 1, the system becomes ferromagnetic, with the Curie temperature  $T_C \approx 56$  K [26].

We note that calculations of the electronic structure of  $LaOFe_{1-x}Co_xAs$  in [30] show that the substitution of Co for Fe leads to a displacement of the Fermi level from its position on the steep side of the curve of the partial density of Fe 3d states into the region of its smooth behavior. This displacement of the Fermi level explains the suppression of the spin-density wave (SDW) transition inherent in the initial state of LaOFeAs as a result of the substitution of Co for Fe atoms.

We now discuss the superconducting properties of FeAs systems in greater detail. How is the superconducting state of the doped compound manifested in experiments? For example, we consider the compound  $\text{SmO}_{1-x}F_x\text{FeAs}$ , in which the highest value of  $T_c = 55$  K was obtained at



**Figure 3.** Manifestation of the superconducting state in the  $\text{SmO}_{0.9}\text{F}_{0.1}\text{FeAs}$  compound in the temperature dependence of (a) electric resistance, (b) magnetic susceptibility  $\chi$ , and (c) the derivative of  $\chi$  with respect to temperature. FC, field-cooling regime; ZFC, zero-field cooling [6].

x = 0.1 [6]. Figure 3 displays the results of three different measurements illustrating a sharp decrease in the electric resistance with decreasing the temperature, an abrupt appearance of a diamagnetic response  $\chi$  in an applied field, and a distinct maximum in the derivative  $d\chi/dT$ . All three anomalies are observed near the same temperature, which is the superconducting transition temperature. The curves shown in Fig. 3 are typical of all superconducting compounds of the FeAs systems.

Together with high values of  $T_c$ , the FeAs-type compounds have very high values of critical fields. For example, we take the results of studying the upper critical field  $H_{c2}$  in a polycrystal sample of LaO<sub>0.98</sub> F<sub>0.11</sub> FeAs with  $T_{\rm c} = 28.2$  K [20]. The field  $H_{\rm c2}$  is evaluated from the data on the temperature dependence of the electric resistance in magnetic fields. Figure 4a presents such data for fields up to 8 T, and Fig. 4b displays  $H_{c2}(T)$  values found from these data. It is seen from Fig. 4b that the width of the resistive transition upon the application of the field is shifted toward lower temperatures, which is characteristic of type-II superconductors. The superconducting transition temperature  $T_{\rm c}(H)$  is determined from the condition that  $\rho(T_{\rm c}, H)$  is equal to a certain fraction (percentage) of the resistance  $\rho_{\rm N}$ in the normal phase for each value of H. The dependences  $T_{\rm c}(H)$  thus determined for  $\rho$  equal to 10% of  $\rho_{\rm N}$  (0.1 $\rho_{\rm N}$ ), 30% of  $\rho_{\rm N}$  (0.3 $\rho_{\rm N}$ ), and 90% of  $\rho_{\rm N}$  (0.9 $\rho_{\rm N}$ ) are shown in Fig. 4b together with the critical fields  $H_{c2}(T)$ . In all cases, the  $H_{c2}(T)$  dependences are linear without any sign of saturation. The slope  $dH_{c2}/dT|_{T=T_c}$  is equal to -0.87 T K<sup>-1</sup> for  $\rho = 0.1\rho_N$ , -1.41 T K<sup>-1</sup> for  $\rho = 0.5\rho_N$ , and -1.59 T K<sup>-1</sup> for  $\rho = 0.9 \rho_{\rm N}$ . In the Bardeen-Cooper-Schrieffer (BCS) theory,  $H_{c2}$  depends on T linearly near  $T_c$  and saturates at T = 0. According to the Werthamer-Helfand-Hohenberg theory [31], we have

$$H_{c2}(0) \approx -0.693 T_{c} \left. \frac{\mathrm{d}H_{c2}}{\mathrm{d}T} \right|_{T=T_{c}}.$$
 (1)

The dashed curves in Fig. 4b show the extrapolation of the experimental curves to the values of  $H_{c2}(0)$  calculated this way. For the resistance  $\rho = 0.9\rho_N$ , the value of  $H_{c2}(0)$  exceeds 30 T. From the well-known Ginzburg–Landau formula for the correlation length  $\xi(0) \approx [\Phi_0/(2\pi H_{c2})]^{1/2}$ , where  $\Phi_0$  is the flux quantum, the following estimates are obtained:  $\xi(0) \approx 48$  Å for  $H_{c2}$  (at  $\rho = 0.1\rho_N$ ),  $\xi(0) \approx 36$  Å for  $H_{c2}$  (at



Figure 4. Temperature dependence of the electric resistance in various magnetic fields (a), and  $H_{c2}$  fields calculated from these data for LaO<sub>0.89</sub>F<sub>0.11</sub>FeAs [20] (b).

 $0.5\rho_{\rm N}$ ), and  $\xi(0) \approx 33$  Å for  $H_{\rm c2}$  (at  $0.9\rho_{\rm N}$ ). These values are comparable with those measured in cuprates at the corresponding values of  $T_{\rm c}$ .

The Hall constant measured using the same sample turned out to be negative (which corresponds to electron charge carriers); the charge carrier concentration was  $\approx 1.7 \times 10^{21}$  cm<sup>-3</sup> at room temperature and  $\approx 1 \times 10^{21}$  cm<sup>-3</sup> at a temperature slightly exceeding  $T_c$  (under the assumption of the existence of a single band for the carriers).

The LaOFeAs compound can be doped not only with fluorine, which substitutes for oxygen, but also with elements that substitute for lanthanum, for example, with potassium. Doping with potassium leads to hole rather than electron carriers. In Ref. [32], a new procedure was suggested for the synthesis of superconducting compounds based on LaOFeAs, which allows doping them with fluorine and potassium simultaneously. The synthesized doubly doped compound La<sub>0.8</sub>K<sub>0.2</sub>O<sub>0.8</sub>F<sub>0.2</sub>FeAs with  $T_c = 28.5$  K had  $H_{c2} \approx 122$  T.

The data given for the sample of LaO<sub>0.89</sub>F<sub>0.11</sub>FeAs are quite typical of the entire series of superconducting compounds of the *REO*<sub>1-x</sub>F<sub>x</sub>FeAs type. For NdO<sub>0.82</sub>F<sub>0.18</sub>FeAs with  $T_c = 51$  K [33], the values of the critical field  $H_{c2}(0)$ estimated using Eqn (1) and the experimentally measured value  $H_{c2}(48 \text{ K}) = 13$  T are in the range 80–230 T. A measurement on a single crystal of the same composition revealed a large anisotropy of  $H_{c2}$  [34]. The values of the critical field in the basal plane and along the tetragonal axis were equal to  $H_{c2}^{ab}(0) \approx 304$  T and  $H_{c2}^c(0) \approx 62-70$  T. The measurements of the compound with Sm confirmed the high values of  $H_{c2}$ . For example, measurements of heat capacity in fields up to 20 T in a sample of SmO<sub>0.85</sub>F<sub>0.15</sub>FeAs with  $T_c = 46$  K showed [35] that  $[dH_{c2}/dT]_{T=T_c} = -5$  T K<sup>-1</sup>, which, according to Eqn (1), yields the estimate  $H_{c2}(0) = 150$  T. For another sample of the composition SmO<sub>0.7</sub>F<sub>0.3</sub>FeAs [36] with  $T_c = 54.6$  K, the estimated value of  $H_{c2}(0)$  was even greater,  $H_{c2} \approx 200$  T.

#### 2.2 Magnetic properties

The stoichiometric REOFeAs compounds are antiferromagnetic. The first indications of the possibility of a magnetic ordering in LaOFeAs came from measurements of the temperature dependence of the electric resistance and magnetic susceptibility, which showed anomalies in the vicinity of  $T \approx 150$  K. At this temperature, a structural transition from the tetragonal to the orthorhombic phase was discovered. It was initially supposed that magnetic ordering also occurs at this temperature. At present, the situation has been clarified by exhaustive neutron diffraction studies performed using the reactor in Oak Ridge (USA) [37]. At  $T \approx 155$  K, there indeed occurs a structural transition with a change in the symmetry from the tetragonal space group P4/nmm to the monoclinic space group P112/n at low temperatures [in some cases, a transition into an orthorhombic phase was observed (space group *Cmma*)].

It turned out that the magnetic phase transition occurs at  $T < T_{\rm N} = 137\,$  K. In the neutron diffraction patterns, magnetic reflections (103), which correspond to doubling the chemical unit cell along the *c*-axis, were revealed. The main result of the study of LaOFeAs is given in Fig. 5a, where the circles and squares show the temperature dependence of the magnetic reflection, which is proportional to the square of the magnetic order parameter, and Fig. 5b displays the magnetic structure that is realized for Fe atoms.

As can be seen from Fig. 5b, the arising magnetic structure represents an antiferromagnetic alternation of ferromagnetic chains in the basal plane and in the direction perpendicular



Figure 5. (a) Intensity of the magnetic Bragg peak in LaOFeAs according to neutron diffraction data as a function of temperature [37]. The experimental points represented by circles and squares correspond to measurements with different diffractometers (BT-7 and HB-1a, respectively). (b) Magnetic structure of stoichiometric *RE*OFeAs compounds (RE = La, Ce, Nd).

to it. This structure is in good agreement with theoretical predictions following from the calculation of the energy band structure of the compound [38]; we note that in this case, the compound itself has a metallic conductivity. In this respect, the magnetic ordering in FeAs compounds differs strikingly from that in cuprates. The stoichiometric cuprate compounds show an usual antiferromagnetic ordering in the basal layers, where the magnetic moments of the Cu atoms are antiparallel to the moments of the nearest neighbors of the copper sublattice; the undoped compounds in this case are Mott insulators.

As was already mentioned, the doping of cuprates leads to the destruction of the long-range magnetic order and the appearance of a superconducting state. An analogous situation also occurs in FeAs systems. Neutron diffraction studies of the doped superconducting compound LaO<sub>1-x</sub>F<sub>x</sub>FeAs ( $T_c = 26$  K) showed the absence of a long-range magnetic order. As in cuprates, the superconductivity here appears near the magnetic phase transition, which indicates the important role of antiferromagnetic fluctuations in the electron pairing.

The magnetic ordering depicted in Fig. 5 was also revealed in another stoichiometric compound, NdOFeAs with  $T_{\rm N} = 141$  K [39]. 1266

In both compounds (RE = La, Nd), the value of the magnetic moment per Fe atom at low temperatures was anomalously small:  $0.36 \mu_B$  for the La compound and  $0.25 \mu_B$  for the Nd compound, whereas the theory predicts  $\sim 2 \mu_B$  [40, 41]. This fact remains unexplained. Certainly, the presence of frustrations (two antiferromagnetic interactions between Fe atoms in the basal plane) must decrease the value of the average magnetic moment, but it is quite difficult to explain its fivefold decrease. There exist, however, calculations of the electron density in the local-density approximation with allowance for Coulomb correlations (LDA + U) with a negative potential U (which must be understood as  $U_{\text{eff}} = U - J$ , where J is the Hund exchange), which leads to a significant decrease in the magnetic moment [42].

Neutron diffraction studies of  $\text{CeO}_{1-x}F_x\text{FeAs}$  [4] partially confirmed the antiferromagnetic structure of other compounds. To be exact, the spins of Fe atoms form ferromagnetic chains with an antiferromagnetic alternation in the basal plane, as in Fig. 5b, but the magnetic structure remains unchanged along the *c*-axis. This seems to be due to the specific behavior of Ce atoms in these compounds, related to the tendency of their electrons toward hybridization with other electrons. Incidentally, the magnetic moments of the Fe atoms in this compound are greater, of the order of  $1 \mu_B$ . The study of the fluorine-doped compound shows a phase diagram analogous to those of the cuprates.

In addition to the above-cited works, we mention Ref. [43], in which the magnetism of the SmOFeAs system was studied using magnetic measurements. In the temperature dependence of the magnetic susceptibility  $\chi(T)$  of the stoichiometric SmOFeAs at  $T \approx 140$  K, an anomaly occurs caused by the development of an antiferromagnetic order. At  $T \approx 6$  K, another peak in  $\chi(T)$  is observed, which indicates the antiferromagnetic ordering in the Sm sublattice. In the doped compound  $SmO_{0.85}F_{0.15}FeAs$ , the antiferromagnetic ordering in the FeAs planes is suppressed, whereas the ordering in the Sm sublattice is retained, although the system is a superconductor with  $T_c = 52$  K. Thus, we have a case where the superconducting and magnetic ordering coexist, although they are realized due to different electrons, those belonging to Fe and Sm atoms. It is interesting to note that the magnetic susceptibility of the SmOFeAs system has a Curie-Weiss contribution from Fe atoms, from which the value of the atomic magnetic moment is estimated to be about  $1.4 \mu_{\rm B}$ .

The problem of the anomalously low values of the average magnetic moment of Fe atoms was discussed in [44, 45]. In Ref. [44], the Mössbauer and muon spin rotation  $(\mu SR)$  spectroscopy were used to thoroughly measure the temperature dependence of sublattice magnetizations and the SDW order parameter in the undoped compound LaOFeAs. From these two measurements, the average magnetic moment of the Fe atom was shown to be equal to  $0.25 \mu_{\rm B}$ . Calculations using the four-band model of an antiferromagnet in the mean-field approximation gave a higher value about  $0.33 \mu_{\rm B}$ , which could be anticipated because the mean-field approximation ignores fluctuations. In Ref. [45], the electronic structure of the LaOFeAs compound and the magnetic moment of Fe atoms were calculated in the local spin-density approximation (LSDA) and generalized gradient approximation (GGA) under the assumption of the existence of different AFM structures. Three types of AFM structures were assumed to exist: AFM-1, AFM-2, and AFM-3, differing in the orientation of the magnetic moments of nearest-neighbor Fe atoms in the basal plane and between the nearest planes; one of the structures (AFM-3), with a doubled magnetic cell along the c-axis, corresponded to the structure that was determined from neutron diffraction experiments. The electronic structure of the compound and the average moments of Fe atoms for each of these three AFM structures were calculated for different volumes of the unit cell of the crystal, i.e., for different applied pressures.

The results proved to be unexpected. At a fixed volume of the cell, the average magnetic moments turned out to be very sensitive to the AFM structure type. In the vicinity of the equilibrium volume, the magnetic moment is substantially less in magnitude, especially for AFM-1 structures. For the actually existing structure AFM-3, the average magnetic moment changes by a factor of three in the interval of pressures  $\pm 5$  GPa (with the cell volume converted into the external pressure). At the pressure 5 GPa, the calculated moments coincide with those measured experimentally. In the range of pressures from -10 to +10 GPa, the magnetic moment of Fe atoms decreases from the maximum possible value of  $2 \mu_{\rm B}$  to almost zero. Hence, with an increase in the negative pressure (expansion of the lattice), a large increase in the magnetic moment is expected. It is interesting to verify this assumption on hydrogenated samples, in which the introduction of hydrogen imitates a negative pressure.

It is remarkable that in a wide range of pressures, the electronic structure changes only a little, whereas the magnetic moment changes quite substantially. This indicates that the magnetic state of the compound (its magnetic structure and the value of the average magnetic moment) results from a delicate balance between the kinetic energy of the system, which determines the electronic structure within the LDA, and the electron interactions. Hence, a description of the FeAs systems in terms of localized spins, for example, within the Heisenberg model, is hardly possible because these compounds are itinerant-electron magnets.

We now discuss the problem of the coexistence of the magnetic order and superconductivity in doped REOFeAs systems. The superconducting state arises near the state of instability of the initial (undoped) compound with respect to magnetic ordering. A question that arises, however, is whether there exist signs of a magnetic order in the range of doping where the superconducting state already exists. No detailed studies on different FeAs compounds have yet been carried out, but there are separate works in which a region of the coexistence of the two phases was discovered. In Ref. [46], it has been shown in the example of  $SmO_{1-x}F_xFeAs$  using  $\mu$ SR spectroscopy that static magnetism extends into the existence range of the superconducting phase. In the range of concentrations  $0.1 \leq x \leq 0.13$ , low-energy spin fluctuations are observed up to x values that correspond to the maximum  $T_c$ . The corresponding phase diagram on the (T, x)plane can be found in Ref. [46].

#### **2.3 Electronic structure**

First-principle calculations of the electronic structure of the LaOFeP compound, in which superconductivity ( $T_c = 4$  K) was revealed for the first time, were performed before the experimental detection of high  $T_c$  in this class of compounds [47]. The calculations for LaOFeAs were carried out almost simultaneously in a number of works [12, 13, 32, 40, 41, 48–50]. The electronic structure of many *REO*FeAs compounds (RE = La, Ce, Sm, Nd, Pr, Y) was also calcu-



Figure 6. Results of LDA calculations of the total and partial densities of states for the LaOFeAs compound [48].



Compound	Fermi surface*	References					
LaOFeAs LaOFeAs LaOFeP LaOFeP NdOFeAs LaONiP	$\frac{2h(\Gamma), h(Z), 2e(M)}{h(Z), AFM is absent}$ $\frac{2h(\Gamma), h(Z), 2e(M)}{ARPES^{**}: 2h(\Gamma), e(M)}$ $\frac{ARPES: h(\Gamma), e(M)}{h(X): 3e(M)}$	[12, 13, 32, 40, 48-52] [41] [47] [54] [53] [53]					
LaONiAs	h(X), 2e(M)	[32]					
* Sheets of the Fermi surface are as follows: $h(\Gamma)$ and $h(Z)$ , hole sheets centered at the $\Gamma$ and Z points; $e(M)$ , electron sheets centered at the M point of the Brillouin zone. ** Data obtained using angle-resolved photoemission spectroscopy.							

lated in Ref. [51]. We here consider the results of calculations in [48], where the method of linearized augmented plane waves (LAPW) within the local-density approximation (LDA) was used. The calculated density of states is shown in Fig. 6, where the partial contributions from d orbitals of Fe and p orbitals of O and As are presented together with the total density of states. The calculated data concerning the Fermi surface are given in Table 2.

Near the Fermi level, there are the d states of Fe, which occupy the range from approximately -2 to +2 eV (the Fermi level is placed at the zero level of energy). A wide region below these d states is filled by p states of As and O. The states due to La atoms lie in the region above the Fermi energy.

The fivefold degenerate Fe d states in the tetrahedral environment of As atoms are split into lower-lying twofold-degenerate  $e_g$  states and threefold-degenerate  $t_{2g}$  states.

The energy band structure is shown in Fig. 7, which is borrowed from the earlier work [47] for the sole reason that the corresponding figure in Ref. [48] is complicated by additional data due to variations in the coordinates of As atoms in the lattice; at the same time, the calculations for LaOFeP in [47] are identical to those for LaOFeAs. As can be seen from Fig. 7, there are 12 dispersion curves. The Fermi level intersects two hole bands, which proceed from the  $\Gamma$  point, and two electron bands, which proceed from the M point. We note the flatness of the curves in the direction  $\Gamma Z$ , which indicates a weak dependence of the hole quasiparticles on the momentum  $k_z$ ; therefore, the Fermi surface (FS) in the vicinity of  $\Gamma$  has a cylindrical shape. The



Figure 7. Energy band structure of the LaOFeP compound [47].



**Figure 8.** Fermi surface of the LaOFeAs compound [48]. Positions of the symmetry points of the Brillouin zone:  $\Gamma(0,0,0)$ , Z(0,0,1/2), X(1/2,0,0), R(1/2,0,1/2), M(1/2,1/2,0), and A(1/2,1/2,1/2) (in  $2\pi/a$  units).

same relates to the FS sheets in the vicinity of the M point (this follows from the flat segment of the curves on the line MA).

Thus, in the case of the LaOFeP compound, two hole cylindrical sheets with their axes in the direction  $\Gamma Z$  and two electron sheets with axes along MA are formed on the FS. This indicates the quasi-two-dimensional nature of the electron states formed by the  $d_{xz}$  and  $d_{xy}$  orbitals. In addition to these four cylindrical sheets, there is a three-dimensional (3D) hole pocket centered at the Z point of the Brillouin zone (Fig. 8). This three-dimensional pocket is formed by  $d_z$  orbitals of Fe hybridized with p states of As and La.

The two hole sheets and the hole pocket compose 80% of the density of states (DOS)  $N(E_{\rm F})$  on the FS. The average electron velocity on them in the *xy* plane is  $0.81 \times 10^7$  cm s<sup>-1</sup>, whereas for the electron sheets, these velocities are  $2.39 \times 10^7$  cm s<sup>-1</sup> and  $0.37 \times 10^7$  cm s<sup>-1</sup>. Hence, there is a high anisotropy of conductivity (equal to approximately 15), which again indicates the quasi-two-dimensional nature of electron states in this material.

The volume occupied by the two electron cylinders (equal to the volume of the hole cylinders) is 0.13 electrons per formula unit. The calculated value of the DOS is  $N(E_{\rm F}) = 2.02 \text{ eV}^{-1}$  per formula unit for both spin direc-



Figure 9. Pockets of the FS restored from ARPES measurements of a single crystal of  $NdO_{1-x}F_xFeAs$  and their correspondence to the FS calculated within the LDA [53].

tions. Hence, LaOFeAs is a conductor with a low concentration of charge carriers and a comparatively high DOS at the Fermi level, in contrast to cuprates. Figures 6-8 display the results of calculations for the stoichiometric compound. Electron doping results in a contraction of the hole pockets, especially of the 3D pocket, thereby enhancing the quasi-twodimensional character of the FS.

Numerous calculations of the electronic structure of a number of compounds of the LaOFeAs type give very close results; they indicate the existence of flat segments in the dispersion curves near the Fermi level in the directions  $\Gamma Z$  and MA, which yield hole and electron cylindrical sheets of the FS, indicating the two-dimensional nature of the electron states in the FeAs layers. These conclusions were verified experimentally using angle-resolved photoemission spectroscopy (ARPES) [53, 54]. In Ref. [53], ARPES spectra were obtained for a single crystal of NdO<sub>1-x</sub> $F_x$ FeAs, which showed the presence of FS pockets near the  $\Gamma$  and M points of the Brillouin zone (Fig. 9), in accordance with the first-principle numerical calculations.

In Ref. [54], ARPES measurements (integrated over angles) of the LaOFeP compound allowed restoring the DOS over a wide range of energies, which proved to be in good agreement with numerical calculations. The angular measurements of photoemission revealed two sheets of the FS around the  $\Gamma$  point and a sheet (apparently degenerate) at the point M. The results of the above-cited works have allowed concluding that the basic features of the electronic structure of LaOFeAs-type compounds are confirmed experimentally.

Recently, the first work appeared devoted to the study of the FS based on measurements of the de Haasvan Alphen effect, with quantum oscillations of magnetization in a magnetic field being measured [55]. As the object of the study, the authors chose the compound LaOFeP (of the same crystal structure as LaOFeAs), with the superconducting transition temperature  $T_c \sim 7$  K. This choice was made because a single-crystal sample, first, of high purity and, second, with a low value of the upper critical field ( $H_{c2} \approx 0.68$  T for the external magnetic field  $B \parallel c$  and 7.2 T for  $B \perp c$ ) was needed in order to suppress the superconducting state in experimentally accessible magnetic fields. The results obtained showed that this compound has two cylindrical hole surfaces centered at the  $\Gamma$  point and two electron surfaces centered at the M point, in complete agreement with the results of the LDA calculation in [47] but with higher effective masses (in the

range  $1.7-2.1 m_{\rm e}$ , where  $m_{\rm e}$  is the mass of a free electron). The electron masses calculated for this compound are of the order of  $0.8 m_{\rm e}$ . Therefore, we have an experimental confirmation (obtained with the aid of different techniques) of the basic conclusions of LDA calculations for FeAs systems.

A comparison of the results of calculations performed by different research groups using different computational methods frequently shows significant discrepancies. These discrepancies are minimal as regards calculations of the energy band structure and the FS, but can lead to contradictory conclusions concerning magnetic properties, in particular, relative to the ground magnetic state of FeAs systems. From the moment of the discovery of superconductivity in FeAs systems, some calculations of the ground state of the prototype compound LaOFeAs predicted both ferromagnetic and antiferromagnetic structures of two types, a staggered type and a stripe type. The latter structure, which was predicted in [56], was revealed experimentally in all compounds of FeAs systems. The small differences in the energy of these structures are caused by the itinerant nature of magnetism in FeAs systems, which is quite sensitive to the details of their electron and crystal structure, in particular, to the position of As atoms determined by the parameter  $z_{As}$ . In Ref. [57], all the properties of LaOFeAs were calculated using four different methods (two of which are pseudopotential) and conclusions were made regarding the prospects and accuracy of each of these methods. For calculating the magnetic properties, and for constructing magnetic phase diagrams, in particular, the LDA method with theoretically determined  $z_{As}$  parameters is recommended, as in Ref. [58].

#### 2.4 Symmetry of the superconducting order parameter

It is very important to know the symmetry and shape (in the momentum space) of the superconducting order parameter (OP) — the gap in the electron spectrum on the FS — because it allows deciding on the mechanism of pairing. Several scenarios have been proposed for explaining the superconductivity mechanism in the new class of superconductors [50, 59–63], with different predictions concerning the symmetry of the OP, of the s, d, and p types. There exist several methods for experimentally determining the superconducting gap and therefore studying the symmetry of the superconducting OP. Most efficient are the spectroscopic methods, in which the current *I* is measured as a function of the voltage applied to the sample and the conductance dI/dV

Compound	$T_{\rm c}, {\rm K}$	Method	Order parameter	References				
$LaO_{1-x}F_xFeAs$	27	PCAR	$\Delta = 2.8 - 4.6$ meV, s type, pseudogap at $T > T_c$	[64]				
La <sub>0.9</sub> F <sub>0.1</sub> FeAs	26	NMR	$1/T_1 \sim 1/T^3$ , pseudogap, zeros*	[65]				
LaO <sub>0.9</sub> F <sub>0.1</sub> FeAs	28	PCAR	$\Delta = 3.9 \text{ meV}, \text{ZBC}^{**}, \text{zeros}$	[66]				
SmO <sub>0.85</sub> F <sub>0.15</sub> FeAs	42	PCAR	$\Delta = 6.67 \text{ meV}, \text{ s type}$	[67]				
SmO <sub>0.85</sub> FeAs	52	Tunnel spectroscopy	$\Delta = 8$ meV, ZBC, zeros	[68]				
SmO <sub>0.9</sub> F <sub>0.1</sub> FeAs	51.5	PCAR	$\Delta_1 = 10.5 \text{ meV}, \Delta_2 = 3.7 \text{ meV}, \text{ZBC}, \text{zeros}$	[69]				
Nd <sub>0.9</sub> F <sub>0.1</sub> FeAs		PCAR	$\Delta_1, \Delta_2, \text{ZBC}, \text{zeros}$	[70]				
NdO <sub>0.9</sub> F <sub>0.1</sub> FeAs	_	Measurements of penetration depth	⊿, s type	[71]				
NdO <sub>0.9</sub> F <sub>0.1</sub> FeAs	53	ARPES	$\Delta = 15 \text{ meV}, \text{ s type}$	[72]				
NdO <sub>0.86</sub> F <sub>0.14</sub> FeAs	48	Tunnel spectroscopy	$\Delta = 9.2$ meV, s type, pseudogap at $T > T_c$	[73]				
NdO <sub>0.85</sub> FeAs	52	PES	Gap on the electron M surface	[74]				
* Zeros on the Fermi surface.								
** Zero-bias conductance.								

Table 3. Investigations of the superconducting order parameter of FeAs-based compounds performed by various methods.

is determined, from which the superconducting gap is then calculated by fitting the experimental curves to theoretical ones. This group of methods includes photoelectron spectroscopy (PES), angle-resolved photoemission spectroscopy (ARPES), and point-contact Andreev reflection (PCAR). There also exist techniques of other types; for example, measurements of the temperature dependence of the penetration depth  $\lambda(T)$  in a superconductor and measurements of the inverse spin-lattice relaxation time  $1/T_1$  allow deciding on the existence of zeros of the superconducting OP on the FS. A line of zeros leads not to the exponential dependence (as in conventional superconductors) but to a power-law temperature dependence  $(1/T_1 \sim T^3)$ . Similar information can also be obtained from measurements of the temperature dependence of the electron heat capacity of a superconductor. The results of studies of the superconducting OP in REOFeAs compounds performed by different experimental methods are given in Table 3.

The first experiments were carried out on polycrystals, for which the interpretation of the results is usually ambiguous and contradictory. On the one hand, nuclear magnetic resonance (NMR) measurements showed that there are two gaps with zeros on the FS [75].On the other hand,  $\mu$ SR measurements indicated the existence of a finite gap at all points of the FS [76]. Point-contact tunnel spectroscopy did not permit answering the question of whether there are zeros in the case of superconducting OPs. After single crystals of SmO<sub>1-x</sub>F<sub>x</sub>FeAs [77] and NdO<sub>0.9</sub>F<sub>0.1</sub>FeAs [78] were grown, the situation somewhat clarified. On the same sample of NdO<sub>0.9</sub>F<sub>0.1</sub>FeAs, measurements were carried out both by ARPES [72] and by studying the penetration depth.

We consider in more detail the results of studying the superconducting OP in compounds with Sm and Nd (with  $T_c$  about 50 K), for which two most informative techniques were used, PCAR and ARPES. In Ref. [67], the polycrystalline compound SmO<sub>0.85</sub>F<sub>0.15</sub>FeAs with  $T_c = 42$  K was investigated. The current *I* through the point contact between a normal metal and a superconductor was measured as a function of the applied voltage *V*. According to the theory (see review [79]), the conductance dI/dV for a conventional superconductor with the s symmetry of the gap  $\Delta$  has a two-peak structure near V = 0; moreover, the peak separation in the spectrum is equal to  $2\Delta$ . Figure 10a exemplifies the spectrum for an Au/Nb contact; the points correspond to experimental data and the solid curve is a theoretical result with fitting parameters. Figure 10b displays

the results of measurements for superconducting  $MgB_2$  (a  $Co/MgB_2$  contact). The four maxima observed indicate the presence of two superconducting gaps, one of which  $(\Delta_{\rm S})$  is smaller than the other  $(\Delta_L)$ . These examples confirm the efficiency of the PCAR method. Finally, Fig. 10c shows the spectrum for the SmO<sub>0.85</sub>F<sub>0.15</sub>FeAs compound, which indicates the existence of only one gap  $\Delta$ . This spectrum was obtained for a specific point contact on a superconductor. In Ref. [67], spectra for 70 point contacts were obtained, which were processed by varying the fitting parameters. The averaged value of  $\Delta$  according to the results of the best fit yields  $2\Delta = 13.34 \pm 0.3$  eV; hence, taking into account that  $T_c = 42$  K, we obtain  $2\Delta/kT_c = 3.68$ , which is close to the value obtained in the BCS theory  $(2\Delta/kT_c = 3.53)$ . Hence, according to the results of this investigation, the superconductor in question has one isotropic gap and is therefore a superconductor of the s type. No zeros have been revealed on the FS. The temperature dependence  $\Delta(T)$  is of the usual BCS type.

This result agrees with the data of the ARPES investigation of another compound, NdO<sub>0.9</sub> $F_{0.1}$ FeAs with  $T_c = 53$  K, performed on a single crystal [72]. The conductance measured using this procedure must also have a two-peak structure if there is only one superconducting gap (Fig. 11). The measurements at various angles to the crystallographic axes of the FeAs plane show a certain anisotropy of the gap (see Fig. 11). The superconducting gap is present everywhere on the FS; its value ( $\Delta = 15 \pm 1.5$  meV) is comparable to the results of the previous measurements of  $\Delta$  for this compound [53]. The data obtained agree with the prediction based on an anisotropic s symmetry of the OP; however, another interpretation cannot be excluded, based on the assumption that the observed anisotropy can arise due to the zeros of the OP caused by the contribution to the pairing from the interaction between different sheets of the FS [53] (see below).

We now return to systems with Sm. The study of  $SmO_{0.9}F_{0.1}FeAs$  ( $T_c = 51.5$  K) using point-contact spectroscopy [69] led to the conclusion that this superconductor has another symmetry of the order parameter, which differs from the symmetry described above (see Ref. [67]). Figure 12 displays the point-contact spectra, which, along with a twopeak structure, involve a three-peak structure with the central peak corresponding to the zero value of the applied potential, V = 0. This indicates the existence of zeros on the FS. The three-peak structure of the spectrum corresponds to coupled Andreev states located inside the superconducting gap. These



**Figure 10.** Spectra obtained by the point-contact spectroscopy method at T = 4.52 K for various superconductors: (a) Nb; (b) MgB<sub>2</sub>; (c) SmO<sub>0.85</sub>F<sub>0.15</sub>FeAs. BTK corresponds to calculations based on the Blonder–Tinkham–Klapwijk model; Z and  $\Gamma$  are the parameters of the BTK model.

peaks are usually called the ZBCPs (zero-bias conductance peaks). We note that no such spectra were revealed in Ref. [67], and hence a conclusion was made that the superconducting OP does not have zeros in Sm-containing superconductors. In Ref. [69], the experimental curves were processed under the assumption of a d symmetry of the OP (Fig. 12a). All theoretical curves in Fig. 12 were obtained by parameter fitting. It follows from the results in Ref. [69] that the superconductor SmO<sub>0.9</sub>F<sub>0.1</sub>FeAs has a nonstandard symmetry of the OP with zeros on the FS and two values of the gap  $\Delta_0$  equal to  $10.5 \pm 0.5$  and  $3.7 \pm 0.4$  meV. The data on the superconducting OP in the *RE*OFeAs system are given in Table 2.

# 3. Compounds of the $AFe_2As_2$ type (A = Ba, Sr, Ca)

#### 3.1 Electronic structure

Following compounds of the LaOFeAs type, which are prototypes for high- $T_c$  superconductors, a number of other compounds have been synthesized, such as BaFe<sub>2</sub>As<sub>2</sub> [8], SrFe<sub>2</sub>As<sub>2</sub> [80], and AFe<sub>2</sub>As<sub>2</sub> (A = K, Cs, Sr) [81], which become superconducting under doping. The discovery of superconductivity with  $T_c = 38$  K in Ba<sub>1-x</sub>K<sub>x</sub>Fe<sub>2</sub>As<sub>2</sub> led to a new surge of interest in studies of systems based on FeAs<sub>4</sub> complexes.



**Figure 11.** Distribution of the magnitude of the superconducting gap over the FS sheet centered at the  $\Gamma$  point according to ARPES studies of a NdO<sub>0.9</sub>F<sub>0.1</sub>FeAs single crystal at T = 20 K [72].

The crystal structure of  $BaFe_2As_2$ , which is shown in Fig. 2 in comparison with the structure of LaOFeAs, is tetragonal (the space group I4/mmn,); it is formed by FeAs planes (the

same as in LaOFeAs) separated by Ba planes. There is only one FeAs plane in the unit cell of LaOFeAs, and two in BaFe<sub>2</sub>As<sub>2</sub>. In BaFe<sub>2</sub>As<sub>2</sub>, the Fe-As spacing is less than that in LaOFeAs; therefore, we can expect a greater Fe d-As p hybridization for BaFe<sub>2</sub>As<sub>2</sub> and, as a result, a broader d band in the electron spectrum. The spacing between the nearestneighbor Fe atoms inside Fe-As layers is also less in BaFe<sub>2</sub>As<sub>2</sub>.

The electronic structure of  $BaFe_2As_2$  was calculated by the LDA method in Refs [82–86]. The results of these calculations are very close; we here give the results of calculations of the total and partial DOS in Ref. [84], where they are represented in comparison with the DOS for LaOFeAs (Fig. 13). We see a large similarity of both the total DOS and the d component of the DOS for both compounds, especially in the energy range near the Fermi level. This could be expected because the Fe atoms have identical surroundings of As atoms, which form tetrahedra around them, in both compounds.

The dispersion curves in the vicinity of the Fermi level in both compounds are also similar, because they are formed predominantly by Fe d states. In BaFe<sub>2</sub>As<sub>2</sub>, there are three hole-like bands near the  $\Gamma$  point and two electron bands, as in LaOFeAs, located near the M point (we note that the Brillouin zones are different for these compounds and the X point for BaFe<sub>2</sub>As<sub>2</sub> should be compared with the M point for LaOFeAs).

In the LDA, the FSs for these compounds are quite similar. Each of them has five sheets (approximately



**Figure 12.** (a) Basis function with the  $d_{x^2-y^2}$  symmetry. (b–f) PCAR spectra for the SmO<sub>0.9</sub>F<sub>0.1</sub>FeAs compound at different point contacts. Squares correspond to experimental data; solid curves show calculations in a theory with fitting parameters based on the assumption of a d symmetry of the OP [69].



Figure 13. The total and partial DOS for LaOFeAs and  $BaFe_2As_2$  compounds in the LDA [84].

cylindrical); three of these (hole-type) are located in the center of the Brillouin zone, and two (electron-type) in its corners.

These theoretical conclusions were experimentally verified on single crystals of  $BaFe_2As_2$  and the potassium-doped superconducting compound  $Ba_{1-x}K_xFe_2As_2$  using ARPES [87, 88]. According to the results in Ref. [87], the FS of undoped  $BaFe_2As_2$  consists of a small round pocket (holetype) centered at the  $\Gamma$  point and of a considerably larger electron pocket centered at the X point.

An uncommon shape of the FS was obtained for the compound  $Ba_{1-x}K_xFe_2As_2$  in Ref. [89]. Along with two concentric hole surfaces around the  $\Gamma$  point, there were revealed electron pockets around X and Y points and four hole 'rods' diverging from them in the  $\Gamma X$  directions, which form a figure in the form of a propeller with the center at the X (Y) point. Therefore, the structure of the FS in  $AFe_2As_2$ compounds is more complex than has been revealed up to now in REOFeAs compounds. This picture was refined in another ARPES study [88]. In the vicinity of the  $\Gamma$  point in BaFe<sub>2</sub>As<sub>2</sub>, three FS sheets appear in accordance with the results of most LDA calculations. But some quantitative discrepancies with the data of numerical calculations were observed, although it was noted that if the Fermi level is shifted down by -0.2 eV, then the results of the LDA calculations agree well with the ARPES data. It was assumed in Ref. [88] that the necessity of such a shift of energies indicates the existence of some correlations that have not been considered in the LDA.

Previous calculations of the electronic structure of the AFe<sub>2</sub>As<sub>2</sub> compound were conducted for the stoichiometric composition. In Ref. [90], systematic calculations were performed of the doped compounds  $Ba_{1-x}K_xFe_2As_2$  with x = 0.25, 0.50, 0.75, and 1.00 using the method of the generalized gradient approximation with Coulomb correlations (GGA + U). One of the problems in the case of previous calculations was the anomalously high value of the magnetic moment of Fe atoms  $(2.07 \,\mu_{\rm B})$  in comparison with the experimental value  $0.87 \,\mu_{\rm B}$  [85]. A similar problem arose in calculating magnetic moments in LaOFeAs systems; it was shown in Ref. [91] that the use of negative values of Usubstantially decreases the magnetic moment of Fe atoms. This idea was developed in Ref. [90] for two-layered systems. For undoped  $BaFe_2As_2$  with  $U_{eff} = -0.5$  eV, an SDW instability of the ground state was obtained with the average magnetic moment of an Fe atom equal to  $0.83 \mu_{\rm B}$ , which is close to the experimental value 0.87  $\mu_{\rm B}$ .

#### 3.2 Superconducting order parameter

ARPES measurements of the superconducting gap were carried out on single crystals of  $Ba_{1-x}K_xFe_2As_2$  in two works [92, 93] that appeared simultaneously. In Ref. [93], a sample with x = 0.40 and  $T_c = 35$  K was investigated. Superconducting gaps of different values were revealed on two hole FSs in the vicinity of the  $\Gamma$  point. The gap found on the inner sheet proved to be slightly anisotropic, varying from 10 to 12 meV with a change in the angle; the gap on the outer sheet was isotropic, approximately equal to 8 meV. In the vicinity of the M point, on the electron sheet of the FS, a gap was revealed, equal to 10 meV at T = 15 K. This gap decreases with an increase in the temperature, being equal to 7 meV at T = 25 K and disappearing at  $T = T_c$ . No zeros in the superconducting gaps on the FS have been found. The authors of Ref. [93] draw the conclusion that a superconducting state with several gaps and the s symmetry of the OP is realized in the compound investigated.

On another single crystal, with x = 0.40 and  $T_c = 37$  K, a thorough ARPES study of the FS and the superconducting gap was carried out [92]. The results are presented in Fig. 14. On the lower plane, the color gradation shows the intensity of quasiparticle peaks on the FS as reconstructed from the measurements of photoelectron spectra. The two bright circles in the center correspond to two hole sheets of the FS (denoted by  $\alpha$  and  $\beta$ ) located near the  $\Gamma$  point. The superconducting gaps on these sheets are isotropic; at low temperatures, they have the values  $\Delta_{\alpha} \approx 12$  meV and  $\Delta_{\beta} \approx 6$  meV. With increasing the temperature, these gaps disappear simultaneously at  $T = T_c$ . On the electron sheet  $\gamma$  in the vicinity of the M point, an isotropic superconducting gap  $\Delta_{\gamma} \approx 12 \text{ meV}$  was revealed. The picture of the superconducting gaps in the compound under consideration is reconstructed in Fig. 14 (the upper plane); the height of the cylinders corresponds to the relative values of the gap on different sheets of the FS. These data agree with the results of gap measurements in the compound Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> with  $T_{\rm c} = 37$  K obtained by the method of infrared spectroscopy



Figure 14. Results of ARPES studies of the FS and superconducting gaps in Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> [92].

in Ref. [94] ( $\Delta \approx 12$  meV) and also with the ARPES data [93] given above.

In Ref. [95], systematic ARPES studies were performed on two compounds:  $Ba_{1-x}K_xFe_2As_2$  ( $T_c = 37$  K) and  $Sr_{1-x}K_xFe_2As_2$  ( $T_c = 26$  K). Two concentric FSs were revealed near the  $\Gamma$  point and one surface near the M point, on which superconducting gaps with a weak anisotropy were found. The gap is maximum ( $\Delta = 12 \pm 2$  meV) on the inner FS near the  $\Gamma$  point; it then decreases on the outer central FS and further in the direction toward the M point, but again increases near the corner of the Brillouin zone. This behavior, along with other experimental facts, agrees with the assumption that the OP has the symmetry of the  $s_{x^2y^2}$  or s<sup>+</sup> type in these superconductors, as in some *RE*OFeAs compounds (see Section 5.3).

The charge-carrier velocity measured on the FS proved to be small, only 0.7 eV Å. Using the relation  $\xi = \hbar V_F/\Delta$ , we establish that the correlation length is  $\xi \leq 20$  Å, which corresponds to ~ 4*a* (*a* is the lattice parameter). Such a low value of  $\xi$  has never been found in superconductors with the phonon pairing mechanism.

In Ref. [95], the dispersion curves of the quasiparticles were also measured, and kinks in the energy ranges of  $40 \pm 10$  and  $18 \pm 5$  meV were revealed. The exchange couplings  $J_1$  and  $J_2$ , which are responsible for the magnetic structure of undoped compounds of this type, are approximately 20-50 meV, which exactly corresponds to the higher-energy kink. The lower kink can well be due to the electron-phonon interaction.

Therefore, it can be stated that in the superconducting compound  $Ba_{1-x}K_xFe_2As_2$ , there exists a multigap superconductivity, apparently with an s symmetry of the order parameter. The value of  $2\Delta/kT_c$  is approximately 7, which indicates the case of tight binding in the theory of superconductivity.

Information on the symmetry of the superconducting OP can also be obtained by measuring the temperature and field dependences of the electron heat capacity. In Ref. [96], such measurements were carried out on a Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> single crystal with  $T_c = 36.5$  K. It was found that the electron heat capacity coefficient  $\gamma(T) = C/T$  is temperature independent and increases almost linearly with the magnetic field *H* at low temperatures. These data indicate that the superconducting OP does not have zeros in this compound. The experimental data fall into a curve that corresponds to the s symmetry of the OP with the gap  $\Delta = 6$  meV. This value corresponds to the smallest gap measured in the ARPES study.

Like the *RE*OFeAs compounds, the  $AFe_2As_2$  two-layers are characterized by high values of the critical fields. Investigations performed on a single crystal of  $(Ba_{0.55}K_{0.45})Fe_2As_2$  ( $T_c = 45$  K) showed [97] that the upper critical field  $H_{c2}$  has a moderate anisotropy; the ratio  $H_{c2}^{ab}/H_{c2}^c$  is approximately equal to 3.5 in the vicinity of  $T_c$ and decreases with decreasing T to 1.5 at  $T \approx 20$  K. The estimation of  $H_{c2}$  for this compound yields  $H_{c2}(T=0)$  is approximately equal to 75 T [97]. At a lower level of doping with potassium (x = 0.23 - 0.4), the anisotropy of the upper critical field was smaller, and the critical fields greater:  $H_{c2}^{ab}/H_{c2}^c \approx 2$ ,  $H_{c2}^{ab}(0) = 300$  T, and  $H_{c2}^c(0) = 210$  T [98].

Electron concentrations in  $AFe_2As_2$  compounds are by an order of magnitude higher than those in LaOFeAs; therefore, the density of the superconducting component in them must also be greater. For superconductors with a low concentra-

tion of charge carriers *n*, there exists a relation [99] between the density  $\rho_s$  and the penetration depth  $\lambda(0)$ ; this is the socalled Uemura plot. For quasi-two-dimensional systems,  $\rho_s \sim 1/\lambda_{ab}^2(0)$ , and this relation is well confirmed in cuprates and doped compounds of the LaOFeAs type. The validity of the Uemura plot was checked on the single crystal Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> with  $T_c = 36.2$  K [100]. Based on the measurements of magnetization curves, the temperature dependence of the lower critical field  $H_{c1}(T)$  was determined and the density of superconducting charge carriers was found from the relation

$$\rho_{\rm s}(T) = \frac{\lambda_{ab}^2(0)}{\lambda_{ab}^2(T)} = \frac{H_{\rm cl}(T)}{H_{\rm cl}(0)} \,.$$

It turned out that the Uemura plot is inapplicable to compounds with a double FeAs layer in the unit cell because of the high density of superconducting carriers.

We have already mentioned that in compounds of the LaOFeAs type, the  $\mu$ SR measurements revealed the possibility of the coexistence of static magnetism and superconductivity [101] in a narrow range of concentrations near the antiferromagnet-superconductor phase boundary. A similar state was also revealed in a  $\mu$ SR study of a single crystal of (Ba<sub>0.55</sub>K<sub>0.45</sub>)Fe<sub>2</sub>As<sub>2</sub> [102]. These studies were continued on single crystals of a number of other compounds, e.g., (Ba<sub>0.5</sub>K<sub>0.5</sub>)Fe<sub>2</sub>As<sub>2</sub> ( $T_c = 37$  K), (Sr<sub>0.5</sub>Na<sub>0.5</sub>)Fe<sub>2</sub>As<sub>2</sub> ( $T_c = 35$  K), and CaFe<sub>2</sub>As<sub>2</sub>, under the pressure up to 10 kbar [103].

ARPES studies of the compound  $Sr_{1-x}K_xFe_2As_2$  [104] showed that an exchange splitting of the electron spectrum due to the SDW structure occurs at the dopant concentration at which the compound is already superconducting, which also indicates the possible coexistence of antiferromagnetism and superconductivity in  $AFe_2As_2$  systems.

#### **3.3 Doping and pressure**

The record high values of  $T_c = 38$  K were obtained as a result of doping BaFe<sub>2</sub>As<sub>2</sub> with potassium; the charge carriers in Ba<sub>1-x</sub>K<sub>x</sub>Fe<sub>2</sub>As<sub>2</sub> compounds are holes, which is confirmed by Hall-effect measurements and which is explainable from the standpoint of the crystal chemistry of this compound. Because of the close values of the ionic radii of Ba and K, the complete substitution of one element for the other is possible in this system, such that the compound (Ba<sub>1-x</sub>K<sub>x</sub>)Fe<sub>2</sub>As<sub>2</sub> can be obtained in the entire range of compositions 0 < x < 1. The measurements showed that superconductivity exists in the entire range of x, but the maximum value  $T_c = 38$  K occurs at x = 0.4 (Fig. 15a).

In Ref. [106], the initial compound BaFe<sub>2</sub>As<sub>2</sub> was doped with cobalt, which substitutes for Fe atoms in FeAs planes. A remarkable result is that the compound obtained was a superconductor with  $T_c = 22$  K. The Hall-effect data show that the charge carriers here are electrons, which can be explained based on the crystal chemistry of the compound. This indicates that FeAs systems substantially differ from cuprates, in which the substitution for Cu atoms in CuO<sub>2</sub> planes suppresses the superconductivity. In the sample of Ba<sub>2</sub>Fe<sub>1.8</sub>Co<sub>0.2</sub>As<sub>2</sub> that was investigated, the substitution of Co for Fe atoms leads to a significant disorder in FeAs planes, which does not suppress the superconductivity, but actually creates it, destroying the AFM order in the original system. These studies were continued in Ref. [106] by the NMR method to show that the compound BaFe<sub>2-x</sub>Co<sub>x</sub>As<sub>2</sub> with



Figure 15. Superconducting transition temperature as a function of the doping level (a) and the pressure applied to  $AFe_2As_2$  compounds (b) (A = Ba, Sr) [105].

 $T_{\rm c} = 22$  K exhibits a pseudogap state with the pseudogap  $\Delta_{\rm PG} \approx 560$  K [107]. We note that a similar situation was earlier revealed in the LaO(Fe, Co)As system [26]. The substitution of sodium for a rare-earth element was also reported in [108], which leads to a high value of  $T_{\rm c}$ . For example, superconductivity with  $T_{\rm c} = 34.7$  K was revealed in Eu<sub>0.7</sub>Na<sub>0.3</sub>Fe<sub>2</sub>As<sub>2</sub> [108].

Analogous results were obtained when doping  $SrFe_2As_2$ with cobalt. Superconductivity with  $T_c = 20$  K was found to exist in the doped compound  $SrFe_{2-x}Co_xAs_2$  in the range 0.2 < x < 0.4 [109]. The existence of superconductivity under the conditions of strong disorder makes the assumption of the p or d symmetry of the superconducting order parameter quite problematic, because it is known that such superconductivity is suppressed by quite small degrees of disorder. The results of LDA calculations for  $x \ge 0.3$  [109] show that the AFM order must be completely suppressed in such a system, thereby creating conditions for the appearance of superconductivity in it.

Upon the complete substitution, for example, of Ni for Fe, a substantial change occurs in the properties of the compound. For example, it was revealed in the case of a single crystal BaNi<sub>2</sub>As<sub>2</sub> [110] that the structural and phase transition at  $T_0 = 130$  K is a first-order transition, the Hall coefficient is negative, and the superconducting transition

temperature is low ( $T_c = 0.7$  K). The upper critical field is anisotropic and has the initial slope  $dH_{c2}^c/dT = -0.19$  T K<sup>-1</sup> and  $dH_{c2}^{ab}/dT = -0.40$  T K<sup>-1</sup>.

Apart from doping, the physical properties of  $AFe_2As_2$ compounds are substantially affected by pressure. It was shown in Ref. [111] that the undoped compound  $SrFe_2As_2$ exhibits a volumetric structural – magnetic phase transition at  $T_0 = 205$  K. Under an applied pressure P, this temperature decreases and, according to estimates,  $T_0$  can decrease to zero at P = 4-5 GPa. At a pressure somewhat exceeding 2.5 GPa, the resistance sharply decreases, revealing a tendency toward the appearance of superconductivity.

Among the unique properties of systems with double FeAs layers, we note the development of superconductivity under the application of pressure to the original compounds  $AFe_2As_2$  (A = Ba, Sr) revealed in Ref. [105]. In SrFe<sub>2</sub>As<sub>2</sub>, superconductivity with  $T_c = 27$  K appears at P = 28 kbar; in BaFe<sub>2</sub>As<sub>2</sub>, superconductivity with  $T_c = 29$  K appears at P = 35 kbar (see Fig. 5). An analogous effect is observed in CaFe<sub>2</sub>As<sub>2</sub> [112], where the superconductivity appears at P = 0.35 GPa. In Ref. [113], a detailed study of this compound was performed by neutron diffraction methods. A surprising phenomenon was discovered: at a fixed temperature (T = 50 K) and the application of pressure, the 'collapse' of the initial tetragonal structure occurs, i.e., an abrupt change in the unit-cell volume (of the order of 5%) is observed without a change in its symmetry. With a further increase in the pressure, the 'compensated' tetragonal structure remains stable and retains the parameters of the unit cell as the applied pressure increases to values of the order of 0.6 GPa. The structural transition from the tetragonal to the orthorhombic phase and the related magnetic transition are suppressed with the appearance of a superconducting phase. It is remarkable that the numerical calculations in the local spin-density approximation (LSDA) show that the magnetic moments vanish upon the transition into the collapsed phase. Neutron diffraction measurements do not reveal them. The collapse also occurs with decreasing the temperature at a fixed pressure. Thus, the following phase diagram on the (T, P) plane is realized for this compound: at  $P \leq 0.35$  GPa and high T, there exists a tetragonal (initial) phase, which passes into the orthorhombic phase of the normal metal. In the domain of the existence of the superconducting phase in a certain range of P at low T, superconductivity exists. The transition to the superconducting phase occurs from the collapsed tetragonal phase. The isostructural phase transition from the usual tetragonal phase to the collapsed phase occurs in the entire range of applied pressures.

We note that pressure-induced isostructural phase transitions were also observed in some strongly correlated systems, for example, in cerium, where they have an electronic nature caused by strong Coulomb correlations. Possibly, the same situation takes place in CaFe<sub>2</sub>As<sub>2</sub>. On the other hand, the authors of Ref. [113] cite a number of works studying systems of the *RE*OFeAs type, in which anomalies in the latticeparameter behavior under the action of pressure were also observed; in particular, in *RE*O<sub>1- $\delta$ </sub>FeAs compounds, correlations between *T*<sub>c</sub> and the cell size were observed. Based on the above data, it can be supposed that oxygen vacancies play a dual role in the formation of superconductivity: they change the number of charge carriers and produce a 'chemical pressure.'

#### 3.4 Magnetism

The magnetic ordering of Fe atoms in stoichiometric compounds  $AFe_2As_2$  (A = Ba, Ca, Sr) has been investigated by neutron diffraction methods in Refs [114-118]. In all these substances, the same magnetic structure (shown in Fig. 5) was revealed. In the basal plane, the magnetic moments of Fe atoms form ferromagnetic chains along one of the orthorhombic axes with the alternation of the direction along the other axis of the basal plane and along the *c*-axis. Thus, there exists a three-dimensional AFM structure with the same motif as in compounds of the LaOFeAs type. The difference is only in the position of the antiferromagnetically coupled planes. These adjacent planes belong to the same unit cell in BaFe<sub>2</sub>As<sub>2</sub> and to two adjacent cells in LaOFeAs. If we remove all atoms except Fe from the crystal structures of both compounds, then the resulting magnetic lattices coincide. Just as in compounds of the LaOFeAs type, the magnetic ordering appears simultaneously (or almost simultaneously) with the structural phase transition from the tetragonal to the orthorhombic phase.

We now turn to some details of the magnetic and structural phase transitions in different AFe2As2 compounds. The first neutron diffraction study BaFe<sub>2</sub>As<sub>2</sub> was performed on a polycrystalline sample [115]. The temperature dependence of the magnetic reflection (101) showed that a magnetic second-order phase transition occurs at  $T_{\rm N} = 143$  K; at the same temperature, a structural transition to the orthorhombic phase is observed. A later study of a single crystal [114] led to other conclusions about these phase transitions (the magnetic structure itself was confirmed). It turned out that the magnetic order disappeared at the same temperature  $T_{\rm N}$ , but no transition of the crystal to the tetragonal phase occurred; neither was it discovered at room temperature. Meanwhile, the magnetic phase transition remains second order. The magnetic moment of the Fe atom in the ordered phase is  $\sim 0.8 \,\mu_{\rm B}$ ; the magnetic moments were aligned along the shortest orthorhombic axis.

Analogous results were obtained in a neutron diffraction study of a CaFe<sub>2</sub>As<sub>2</sub> single crystal [116]. The structural transition was fixed at T = 172.5 K upon cooling and at T = 173.5 K upon heating, but the temperature hysteresis (~ 1 K) proved to be much less than that for BaFe<sub>2</sub>As<sub>2</sub>. The magnetic transition to the same magnetic structure (see Fig. 5) occurs simultaneously with the structural transition. The magnetic moment of Fe atoms upon saturation was ~ 0.81  $\mu_{\rm B}$ , as in BaFe<sub>2</sub>As<sub>2</sub>.

A neutron diffraction study performed on a single crystal of SrFe<sub>2</sub>As<sub>2</sub> [117] revealed a simultaneous occurrence of a structural transition and a magnetic order at  $T_0 = 220$  K, with the formation of the magnetic structure shown in Fig. 5. These results agree with the data of the neutron diffraction study of a polycrystalline sample [118], for which the temperature of both phase transitions was found to be  $T_0 = 205$  K and the magnetic moment at Fe atoms ~ 1  $\mu_{\rm B}$ .

Thus, in all the  $AFe_2As_2$  compounds that have been investigated, the same magnetic structure was revealed, which appeared simultaneously with the structural phase transition. An analogous situation occurs for compounds of the LaOFeAs type. This means that there is a single mechanism of magnetic ordering in all compounds built of FeAs planes, regardless of the nature of the planes (formed by other atoms) that separate them. In all such compounds, strong coupling of the magnetic moments of Fe atoms with structural distortions exists. The observed antiferromagnetic structures can be described in the framework of the Heisenberg model with effective exchange couplings: the respective antiferromagnetic couplings  $J_1$  and  $J_2$  between nearest and next-tonearest neighbors in the basal plane and the coupling  $J_z$  between the planes [119–121]. When  $J_1 < 2J_2$ , the ground state of the model is a collinear antiferromagnet. When  $J_1/J_2 > 0.05$ , the magnetic ordering and structural transition temperatures are close, which is also the case with FeAs structures.

The instability of stoichiometric compounds of some other compositions was also revealed using the Mössbauer effect on <sup>57</sup>Fe nuclei from anomalies in the thermodynamic and transport properties of these compounds. For example, a structural and a magnetic phase transition in EuFe<sub>2</sub>As<sub>2</sub> was observed at  $T_0 = 190$  K [122]. Upon doping with potassium, the magnetic transition in the Eu<sub>1-x</sub>K<sub>x</sub>Fe<sub>2</sub>As<sub>2</sub> system was suppressed and superconductivity appeared (with a rather high value  $T_c = 32$  K) [123]. The magnetic transitions revealed by neutron diffraction and other methods and the connection between their suppression as a result of doping and the appearance of superconductivity seem to be a common property of all  $AFe_2As_2$  systems.

In some AFe<sub>2</sub>As<sub>2</sub> compounds, effects related to the lowtemperature magnetic ordering of rare-earth atoms that serve as A atoms are observed. These effects manifest themselves most strongly in EuFe<sub>2</sub>As<sub>2</sub> compounds, because Eu atoms have a large magnetic moment [124]. The stoichiometric compound EuFe<sub>2</sub>As<sub>2</sub> has an SDW structure in the FeAs sublattice. Near  $T_{\rm N} \approx 20$  K, an AFM order appears in the Eu sublattice; as a result of the strong coupling with the Fe sublattice, both magnetic orders noticeably affect each other. The EuFe<sub>2</sub>As<sub>2</sub> compound and doped La-containing compounds exhibit metamagnetism; in these compounds, a phase transition from the AFM to the FM state occurs under the effect of a magnetic field. In Ref. [125], phase diagrams of the initial and doped compounds on the (T, H) plane have been constructed; in fields of the order of 1 T, an AFM-FM transition occurs.

The EuFe<sub>2</sub>As<sub>2</sub> compound is also very sensitive to the applied pressure. We have already mentioned the induction of superconductivity by pressure in  $AFe_2As_2$  compounds with A = Ba, Sr, and Ca. In EuFe<sub>2</sub>As<sub>2</sub>, the pressure also reduces the  $T_0$  temperature to 90 K at P = 2.3 GPa; the arising superconducting phase has  $T_c = 29.5$  K, in complete analogy with  $AFe_2As_2$  compounds. A remarkable fact is that the pressure does not decrease the Néel temperature of the AFM ordering of the Eu sublattice, and this ordering is preserved in the superconducting phase [126], resembling the phenomenon of reentrant superconductivity in Chevrel phases.

We finally note Ref. [127], where the spectrum of dynamic spin fluctuations in the compound SrFe<sub>2</sub>As<sub>2</sub> was measured by the method of inelastic neutron scattering. At T = 7 K, the spectrum of magnetic excitations  $S(\mathbf{Q}, \omega)$  consists of a Bragg peak, a spin gap ( $\Delta \leq 6.5$  meV), and distinct spin-wave excitations. Using the Heisenberg model, the authors of Ref. [127] estimated exchange integrals for the nearest and next-to-nearest neighbors as  $J_{1a} + 2J_2 = 100 \pm 20$  meV. Under heating to  $T_{\rm N} = 220$  K, the gap decreases to zero, and critical scattering by spin fluctuations is observed.

We now return to doped compounds of the  $(Ba_{1-x}K_x)Fe_2As_2$  type. The doping of the initial compound  $BaFe_2As_2$  with potassium reduces the structural and mag-

netic transition temperature  $T_0$ . At a certain value of the parameter x, superconductivity appears, as can be seen from Fig. 15a. A more thorough study of the magnetic state in phases that are close to the superconducting state showed that there exists a region of the coexistence of the antiferromagnetic and superconducting states. This distinguishes two-layer systems from systems of the LaO<sub>1-x</sub>F<sub>x</sub>FeAs type, in which, as we see, superconductivity appears when the AFM ordering completely disappears.

A study of different compounds within the entire class of AFe<sub>2</sub>As<sub>2</sub> systems showed that superconductivity appears upon doping those initial compounds that exhibit an SDW instability. Suppression of the SDW instability by doping creates conditions for the appearance of the superconducting state. In this connection, it is interesting to note that a new compound, BaRh<sub>2</sub>As<sub>2</sub>, which has the same crystal structure as the AFe<sub>2</sub>As<sub>2</sub> compounds, was thoroughly investigated in [128]. In BaRh<sub>2</sub>As<sub>2</sub>, there are RhAs layers, in which Rh atoms are surrounded by a tetrahedron of As atoms. The electronic properties of this compound are similar to the electronic properties of all other AFe<sub>2</sub>As<sub>2</sub> compounds. Nevertheless, no signs of structural or AFM ordering have been found in RhFe<sub>2</sub>As<sub>2</sub> in the temperature range from 2 to 300 K. It seems to be quite important to investigate doped compounds in order to determine the possibility of the existence of superconductivity in them. This could elucidate the role of the antiferromagnetic instability in FeAs systems in the formation of the superconducting state.

#### 4. Compounds of the LiFeAs and FeSe types

#### 4.1 Electronic structure and superconductivity in LiFeAs

Recently, a new structural type of FeAs compounds was revealed, in which superconductivity with a sufficiently high  $T_c$  was found. It was reported in Ref. [10] that the undoped compound LiFeAs is a superconductor with  $T_c = 18$  K. Detailed structural and physical studies of a single crystal [9] showed that LiFeAs belongs to the class of compounds built of FeAs layers of the same type as in the case of *RE*OFeAs and *A*Fe<sub>2</sub>As<sub>2</sub>; the FeAs planes are there separated by Li planes. In contrast to the known undoped compounds *RE*OFeAs and *A*Fe<sub>2</sub>As<sub>2</sub>, LiFeAs exhibits no magnetic instability, and the superconductivity exists in it in the absence of any doping. The charge carriers in LiFeAs are electrons; the upper critical field is  $H_{c2}(0) > 80$  T.

The crystal structure of LiFeAs belongs to the space group P4/nmm, in which the atoms occupy the positions Fe(2a)(0,0,0), Li(2b)(0,0,1/2), and  $As(2c)(0,1/2, z_{As})$ ; the lattice parameters are a = 2.76 Å and c = 6.28 Å. Based on these data, a complete LDA calculation of the electronic structure was performed in [129] and the total and partial DOS, the energy band spectrum, and the FS were estimated. All these characteristics turned out to be very close to those known for the previously studied *RE*OFeAs and *A*Fe<sub>2</sub>As<sub>2</sub> compounds, thus confirming the assumption that the electronic properties of FeAs-type compounds are mainly determined by the FeAs layers.

Because the coordinate  $z_{As}$  of As atoms in the unit cell is not known exactly, the authors of Ref. [129] optimized the crystal structure by the LAPW method and obtained  $z_{As} = 0.21696$ . This value was used to calculate the abovementioned characteristics of the electronic structure. The FS



Figure 16. Dispersion curves near the Fermi level for three types of FeAs structures calculated in the LDA [129].

of LiFeAs consists of two cylindrical hole sheets located in the center of the Brillouin zone and of two electron sheets in its corners, just as in all other previously calculated compounds. The difference consists in the fact that in LiFeAs, the two sheets at the  $\Gamma$  point are substantially closer to each other.

Figure 16 (borrowed from Ref. [129]) allows comparing the calculated dispersion curves near the Fermi level for all three types of FeAs systems. In all these compounds, there are hole bands in the vicinity of the  $\Gamma$  point and electron bands in the vicinity of the M point, which agrees with the abovedescribed FS.

The electronic structure was also calculated for a hypothetical compound LiFeSb under the assumption that it has the same crystal structure as LiFeAs. It is natural that the calculated electronic structure turned out to be very similar to that of LiFeAs and even had the same SDW instability. If it were possible to synthesize this substance and suppress its magnetic ordering by doping, we could expect the appearance of superconductivity in it. This superconductor would have an important advantage over LiFeAs: it would not contain toxic As [130].

#### 4.2 Superconductivity in FeSe-type compounds

The discovery of superconductivity with  $T_c = 8$  K in the compound FeSe<sub>1-x</sub> [131] gave birth to a new class of superconductors with an FeAs-type structure. Although these compounds contain Se (or S and Te, which were used later) instead of As, they belong to the same class of layered tetragonal structures with the space group P4/nmm. The FeSe compound consists of layers formed by FeSe<sub>4</sub> groups, in which each of the Fe atoms forming a square lattice is surrounded by a tetrahedron of Se atoms. The other two compounds (FeS and FeTe) have the same crystal structure.

The interest in compounds of the FeSe type arose in connection with the discovery of their superconductivity with the high value  $T_c = 27$  K under the pressure 1.48 GPa [11]; with an increase in pressure,  $T_c$  increases at a high rate (9.1 K GPa<sup>-1</sup>). The upper critical field  $H_{c2}$  was estimated to be ~ 72 T at P = 1.48 GPa.

The similarity of the crystal structures of the new compounds and those of the FeAs systems leads to a similarity of their electronic structures. Calculations by the LAPW method [132] reveal the same features in the DOS in FeSe, FeS, and FeTe compounds as those found in FeAs systems. Near the FS, the Fe 3d states prevail and the electron spectrum is quasi-two-dimensional. The FS is multisheeted. At the  $\Gamma$  point, there are two small hole-type pockets (cylinders), and two electronic cylinders exist in the corner of the Brillouin zone.

Thus, the class of high-temperature superconductors in FeAs systems is progressively enlarging; together with *RE*OFeAs, *A*Fe<sub>2</sub>As<sub>2</sub>, and LiFeAs, we now have the structure of a fourth, FeSe, type, consisting of only FeSe<sub>4</sub> layers, in which the As  $\rightarrow$  Se replacement does not significantly affect the electronic structure; this allows including it in the general class of FeAs systems.

The superconducting state in FeSe was studied by <sup>77</sup>Se NMR [133]. The measurements of the nuclear spin-lattice relaxation rate  $1/T_1$  at temperatures below  $T_c = 8$  K showed a  $1/T_1 \sim T^3$  behavior without a coherence peak, which was interpreted in [133] as an argument in favor of the existence of an unconventional superconducting OP with zeros on the FS, as in the case of LaO<sub>1-x</sub>F<sub>x</sub>FeAs and LaO<sub>0.6</sub>FeAs compounds [22, 65, 134]. Of course, this result can also be interpreted as was discussed above, as an s<sup>+</sup> superconductivity in the presence of nonmagnetic impurities.

In the normal state at temperatures up to  $T \sim 100$  K, another behavior was revealed,  $1/T_1 \sim \text{const}$ , indicative of a Fermi-liquid state of the compound, which distinguishes it from the compounds investigated in Ref. [65]. This feature of the FeSe compound, which differs from compounds of the LaOFeAs type, should relate to the fact that neither magnetic nor structural phase transitions are observed in FeSe, and hence the system is far from the magnetic instability and the role of magnetic fluctuations in the formation of superconductivity therefore seems to be insignificant. This factor is probably responsible for the low value of  $T_c$  in this compound. The experimentally observed increase in  $T_c$  with increasing the pressure is a fundamental problem to be solved in the theory; it is directly related to the explanation of the superconductivity mechanism in systems of this class formed by Fe layers.

The appearance of superconductivity upon doping FeSe with cobalt or with sodium was reported in [135]. The compositions  $Fe_{0.92}Co_{0.08}Se$  and  $Na_{0.1}FeSe$  are superconductors with  $T_c \approx 8.3$  K. Upon doping with cobalt, as in compounds of other classes of FeAs systems, a substitution for Fe atoms in FeAs layers occurs. However, it is for the first time that superconductivity has been induced as a result of intercalating a dopant (Na<sup>+</sup>) between FeAs layers.

Interesting results were obtained in the doped compound  $Fe(Se_{1-x}Te_x)_{0.82}$  [136]. Superconductivity was found in the entire range of  $T_e$  concentrations except for a small vicinity of x = 1. With changing the composition, two different superconducting phases were observed, one in the range of concentrations  $0 \le x \le 0.15$  with  $T_c \approx 9$  K, and the other in the range 0.3 < x < 1 with  $T_c^{max} = 14$  K at  $x \approx 0.6$ . As x approaches 1, the second phase gradually disappears and the system approaches a state of the ferromagnetic or antiferromagnetic instability. In the range 0.15 < x < 0.3, both phases coexist; this range is characterized by an unconventional structural transition near  $x \approx 0.2$ , in which two structural phases coexist.

#### 5. Theoretical models

#### 5.1 Theoretical problems

We first summarize the results of the available experimental studies of the new class of superconductors. Similarly to the cuprates, FeAs systems are quasi-two-dimensional materials with an AFM long-range order in the case of stoichiometric compositions. Superconductivity appears if they are doped with electrons [3-5, 137] or holes [8].

But in contrast to cuprates, which are insulators in the stoichiometric composition, FeAs systems are metallic in this state. In cuprates, an important role is played by local Coulomb interactions, which lead to the Mott-Hubbard metal-insulator transition, whereas the FeAs systems should be regarded as itinerant-electron magnets, in which a Fermi-liquid behavior occurs [138, 139] and is preserved at all levels of doping, including the initial undoped compounds. They are characterized not by the antiferromagnetism of localized spins but by a CDW-type charge ordering. One argument in favor of this concept is the smallness of the magnetic moments of Fe atoms, which are equal to 12-16% of the theoretically predicted value  $2\mu_{\rm B}$ .

The electronic structure of FeAs systems was reliably explained using LDA calculations and was verified experimentally. The states of the electron spectrum near the Fermi level are formed by  $d_{zy}$  and  $d_{zx}$  orbitals of the two Fe ions present in the unit cell. The hybridization of these states generates four bands of charge carriers, two of which are holetype and two are electron-type. The FS is four-sheeted; it is formed by two cylindrical sheets centered near the  $\Gamma$  point, which belong to the holes, while the other two sheets, centered at the M point of the Brillouin zone, belong to the electrons. This picture is preserved for most compounds, both stoichiometric and doped.

It is clear, by analogy with cuprates, that in the formation of superconductivity with such high values of  $T_c$  in FeAs systems, an important role must be played by fluctuations of the magnetic order with wave vectors **q** that lie near the wave vector **Q** =  $(\pi, \pi)$  of the SDW structure. The first problem to be solved in theory is to elucidate the nature of the electron – electron interaction, which is responsible for the formation of the magnetic long-range order and the superconducting order parameter.

Experimental studies of the superconducting-gap symmetry have given contradictory results, even in the case of single crystals of a good quality. Some experiments distinctly show a nonzero superconducting gap on the entire FS [64, 66, 71, 77, 93, 140-143] and an s symmetry of pairing [144], whereas others indicate the existence of a line-node gap [22, 75, 145, 146].

Experiments using three different techniques (PCAR [64, 77, 140], ARPES [72, 93, 141], and measurements of the penetration depth  $\lambda(T)$  [71, 142, 143]) indicate the absence of zeros for the superconducting gap, i.e., the three different procedures lead to qualitatively the same result. Measurements of the spin-lattice relaxation rate  $1/T_1$  in NMR experiments [22, 75, 145, 146] show its power-law temperature dependence,  $1/T_1 \sim T^{\alpha}$ , where  $\alpha = 2.5-3$ . This behavior of  $1/T_1$  is interpreted as evidence in favor of the presence of a d-type pairing, which leads to the appearance of zeros in the gap on the FS, leading to the  $1/T_1 \sim T^3$  dependence. But in the 'dirty' limit, this dependence is replaced by the dependence  $1/T_1 \sim T$  because the line of zeros is divided

into fragments due to scattering on impurities. It was shown in Refs [147, 148] that in a superconductor with a special s<sup>+</sup> symmetry of the order parameter, the nonmagnetic impurities radically change the behavior of  $1/T_1$  depending on the temperature, which comes close to the  $1/T_1 \sim T^3$  law. This new type of symmetry suggested in [59] appears when there are two sheets of the FS separated by an antiferromagnetic vector **Q** and the gap on them has opposite signs; i.e., when the gap vanishes in passing from one sheet to another (not on the FS but between the sheets); the  $s^+$  symmetry is also discussed in Refs [50, 149, 150]. The explanation of the power law for the  $1/T_1$  evolution suggested in those works is an alternative to the explanations suggested by NMR experiments, which seem to indicate that there is a superconductor with the s<sup>+</sup> symmetry of pairing, containing a sufficiently high concentration of nonmagnetic impurities.

The primary problem therefore consists in formulating a model of FeAs systems that would allow obtaining an electronic structure with hole and electron sheets on the FS that are centered at the  $\Gamma$  and M points of the Brillouin zone and, in addition, would admit a solution of the equations for the gap with different signs on the hole and electron sheets.

#### 5.2 The minimal two-band model

In accordance with LDA calculations and experimental data, the electronic structure of FeAs systems near the Fermi energy is characterized by two hole pockets near the  $\Gamma$  point and two electron pockets near the M point of the Brillouin zone. The size of the hole and electron pockets is approximately the same. Such a structure is characteristic of the majority of FeAs compounds that have been investigated.

This picture might be simplified, because in order to understand the physics of these systems, it suffices to consider only two bands corresponding to holes near the  $\Gamma$  point and electrons near the M point (Fig. 17). Such a 'minimal' model was suggested in [138]. A more realistic model, which includes four bands, may be needed for the description of magnetic ordering, in particular, when determining the orientation of magnetic moments of Fe atoms that belong to a given unit cell [148].



Figure 17. Minimal two-band model for FeAs systems [148].

The minimal model was used in a number of theoretical studies [138, 148, 151, 152]. In our opinion, the most complete analysis of the physical consequences following from the minimal model is contained in paper [148], whose results we briefly reproduce here.

We write the initial Hamiltonian of the model such that the hybridization of two orbitals on the lattice and the Coulomb interaction of electrons in the same and in different orbitals are taken into account. We represent this Hamiltonian as the sum of two terms:

$$H = H_0 + H_{\text{int}},$$

$$H_0 = \sum_{\mathbf{k}\sigma} \left[ \varepsilon_{1\mathbf{k}} \Psi_{1\mathbf{k}\sigma}^+ \Psi_{1\mathbf{k}\sigma} + \varepsilon_{2\mathbf{k}} \Psi_{2\mathbf{k}\sigma}^+ \Psi_{2\mathbf{k}\sigma} + \Gamma_{\mathbf{k}} (\Psi_{1\mathbf{k}\sigma}^+ \Psi_{2\mathbf{k}\sigma} + \Psi_{2\mathbf{k}\sigma}^+ \Psi_{2\mathbf{k}\sigma}) \right], \qquad (2)$$

$$H_{\text{int}} = \frac{U_{11}}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4 \sigma \sigma'} \left[ \Psi_{1\mathbf{k}_1 \sigma}^+ \Psi_{1\mathbf{k}_2 \sigma'}^+ \Psi_{1\mathbf{k}_3 \sigma'}^+ \Psi_{1\mathbf{k}_4 \sigma} + \Psi_{2\mathbf{k}_1 \sigma}^+ \Psi_{2\mathbf{k}_2 \sigma'}^+ \Psi_{2\mathbf{k}_3 \sigma'}^+ \Psi_{2\mathbf{k}_4 \sigma} \right] +$$

+ 
$$U_{12} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4 \sigma \sigma'} \Psi^+_{1 \mathbf{k}_1 \sigma} \Psi^+_{2 \mathbf{k}_2 \sigma'} \Psi_{2 \mathbf{k}_3 \sigma'} \Psi^+_{1 \mathbf{k}_4 \sigma},$$
 (3)

where  $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{k}_4$ ,  $\Psi_{1\mathbf{k}\sigma}^+$  and  $\Psi_{2\mathbf{k}\sigma}^+$  are the Fourier components of the operators of electron creation in orbitals 1 and 2,  $\varepsilon_{1\mathbf{k}}$  and  $\varepsilon_{2\mathbf{k}}$  are the Fourier components of the matrix elements of electron transfer over the lattice,  $\Gamma_{\mathbf{k}}$  is the parameter of orbital hybridization, and  $H_{\text{int}}$  contains two parameters, the Coulomb interaction of electrons  $U_{11}$  in the same orbital and  $U_{12}$  in two different orbitals.

The quadratic form  $H_0$  can be diagonalized by a linear transformation of the initial operators to fermionic operators  $h_{\mathbf{k}\sigma}$  and  $e_{\mathbf{k}\sigma}$  that respectively correspond to holes and electrons of the minimal model:

$$\Psi_{1\mathbf{k}\sigma} = \cos\theta_{\mathbf{k}}h_{\mathbf{k}\sigma} + \sin\theta_{\mathbf{k}}e_{\mathbf{k}\sigma},$$

$$\Psi_{2\mathbf{k}\sigma} = \cos\theta_{\mathbf{k}}e_{\mathbf{k}\sigma} - \sin\theta_{\mathbf{k}}h_{\mathbf{k}\sigma},$$
(4)

where  $\theta_{\mathbf{k}}$  is defined by the condition

$$\tanh 2\theta_{\mathbf{k}} = \frac{2\Gamma_{\mathbf{k}}}{\varepsilon_{2\mathbf{k}} - \varepsilon_{1\mathbf{k}}} \,. \tag{5}$$

After transformations (4),  $H_0$  diagonalizes:

$$H_0 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}^h h_{\mathbf{k}\sigma}^+ h_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}^e \varepsilon_{\mathbf{k}\sigma}^+ \varepsilon_{\mathbf{k}\sigma} \,, \tag{6}$$

where

$$\varepsilon_{\mathbf{k}}^{\mathrm{h,e}} = \frac{\varepsilon_{1\mathbf{k}} + \varepsilon_{2\mathbf{k}}}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_{1\mathbf{k}} - \varepsilon_{2\mathbf{k}})^2 + 4\Gamma_{\mathbf{k}}^2} \tag{7}$$

is the energy of fermionic excitations.

Depending on the values of the initial parameters  $\varepsilon_{1k}$ ,  $\varepsilon_{2k}$ , and  $\Gamma_k$  and of the chemical potential  $\mu$ , Eqn (7) describes different situations. We should select those parameters at which the two sheets of the FS (which satisfy the conditions  $\varepsilon_k^h = \mu$  and  $\varepsilon_k^e = \mu$ ) form small circles near the  $\Gamma$  point and near the M point, which correspond to the hole and electron quasiparticles of the model of FeAs compounds (and the radii of these circles would be nearly equal). In this case, a nesting between the hole and electron sheets is achieved with the appropriate wave vector  $\mathbf{Q} = (\pi, \pi)$  (see Fig. 17).

The analysis in [148] shows that this is the case if the hybridization term prevails and has the property  $\Gamma_{\mathbf{k}} = \Gamma_{\mathbf{k}+\mathbf{Q}}$ . We then have  $\varepsilon_{\mathbf{k}}^{h} \approx \Gamma_{\mathbf{k}} \approx -\varepsilon_{\mathbf{k}+\mathbf{Q}}^{e}$  and  $\theta_{0} \approx \theta_{\mathbf{Q}} \approx \pi/4$ . In this case,  $\varepsilon_{\mathbf{k}}^{h}$  describes holes with the maximum energy at the point  $\Gamma = (0, 0)$  and  $\varepsilon_{\mathbf{k}}^{e}$  describes electrons with the minimum energy at the point  $\mathbf{M} = (\pi, \pi)$ . In other words, the summation over  $\mathbf{k}$  is performed in expression (6) over small vectors  $\mathbf{k}$  in the first term and over a small vicinity of the point  $\mathbf{k} = \mathbf{Q}$  in the second term.

After linear transformation (4), the Hamiltonian  $H_{\text{int}}$  becomes

$$\begin{split} H_{\rm int} &= U_1^{(0)} \sum h_{\mathbf{k}3\sigma}^+ e_{\mathbf{k}4\sigma'}^+ e_{\mathbf{k}2\sigma'} h_{\mathbf{k}1\sigma} \\ &+ U_2^{(0)} \sum e_{\mathbf{k}3\sigma}^+ h_{\mathbf{k}4\sigma'}^+ e_{\mathbf{k}2\sigma'} h_{\mathbf{k}1\sigma} \\ &+ \frac{U_3^{(0)}}{2} \sum (e_{\mathbf{k}3\sigma}^+ e_{\mathbf{k}4\sigma'}^+ h_{\mathbf{k}2\sigma'} h_{\mathbf{k}1\sigma} + \text{h.c.}) \\ &+ \frac{U_4^{(0)}}{2} \sum e_{\mathbf{k}3\sigma}^+ e_{\mathbf{k}4\sigma'}^+ e_{\mathbf{k}2\sigma'} e_{\mathbf{k}1\sigma} \\ &+ \frac{U_5^{(0)}}{2} \sum h_{\mathbf{k}3\sigma}^+ h_{\mathbf{k}4\sigma'}^+ h_{\mathbf{k}2\sigma'} h_{\mathbf{k}1\sigma} \,. \end{split}$$
(8)

The quantities  $U_i^{(0)}$  (i = 1, ..., 5) are linear combinations of the Coulomb parameters  $U_{11}$  and of the quantities that depend on  $\theta_{\mathbf{k}}$  at the two points  $\mathbf{k} = 0$  and  $\mathbf{k} = \mathbf{Q}$ . We write them in the above case where the term  $\Gamma_{\mathbf{k}}$  dominates and  $\theta_0 = \theta_{\mathbf{Q}} = \pi/4$ . Then

$$U_1^{(0)} = U_4^{(0)} = U_5^{(0)} = \frac{U_{11} + U_{12}}{2} ,$$

$$U_2^{(0)} = U_3^{(0)} = \frac{U_{11} - U_{12}}{2} .$$
(9)

The Coulomb parameters  $U_{11}$  and  $U_{12}$  are positive; therefore, the quantities  $U_1^{(0)}$ ,  $U_4^{(0)}$ , and  $U_5^{(0)}$ , which respectively represent the hole–electron, electron–electron, and hole–hole interactions, are also positive. As regards the parameters  $U_2^{(0)}$  and  $U_3^{(0)}$ , which describe the exchange and Hund interactions, they can have different signs. It is most probable that the intraorbital Coulomb interaction prevails over the interorbital one; therefore, the terms  $U_2^{(0)}$  and  $U_3^{(0)}$ can also be assumed to be positive. In FeAs systems, the electron correlations are apparently weak (or, at most, moderate); therefore, it can be assumed that  $u_i = U_i N(E_F) < 1$  and the term  $H_{int}$  can be considered in the perturbation theory framework.

#### 5.3 The s<sup>+</sup> symmetry of the order parameter

We first consider the problem of the appearance of different OPs in the system with Hamiltonian (8) in the mean-field approximation. In linearized Hamiltonian (8), the following terms appear:

$$\Delta_{\rm SDW} \sum_{\mathbf{k}} h_{\mathbf{k}\alpha}^+ \sigma_{\alpha\beta}^z e_{\mathbf{k}+\mathbf{Q}\beta} \,, \tag{10}$$

$$\Delta_{\rm CDW} \sum_{\mathbf{k}} h_{\mathbf{k}\alpha}^+ \delta_{\alpha\beta} e_{\mathbf{k}+\mathbf{Q}\beta} \,, \tag{11}$$

$$\Delta_{\rm SC}^{\rm h} \sum_{\mathbf{k}} h_{\mathbf{k}\alpha} \sigma_{\alpha\beta}^{\gamma} h_{-\mathbf{k}\beta} + \Delta_{\rm SC}^{\rm e} \sum_{\mathbf{k}} e_{\mathbf{k}+\mathbf{Q}\alpha} \sigma_{\alpha\beta}^{\gamma} e_{-\mathbf{k}-\mathbf{Q}\beta} \,. \tag{12}$$

In expressions (10)–(12), summation over **k** is performed over small vectors **k**, and hence the quasiparticles in the vicinity of the  $\Gamma$  and **M** points are taken into account. The quantities  $\Delta_{\text{SDW}}$ ,  $\Delta_{\text{CDW}}$ ,  $\Delta_{\text{SC}}^{\text{h}}$ , and  $\Delta_{\text{SC}}^{\text{e}}$  are the order parameters of the spin-density wave (SDW), charge-density wave (CDW), and Cooper pairing of the s type (SC) on holes (h) and electrons (e).

The linearized equations for the OP imply conditions for the existence of their nonzero solutions, which determine the temperatures  $T_{SDW}^{(r,i)}$ ,  $T_{CDW}^{(r,i)}$ , and  $T_{SC}^{(s,s^+)}$  of the appearance of the corresponding instabilities, where the superscripts r and i correspond to the real and imaginary order parameters for the SDW or CDW instability, and the superscripts s and s<sup>+</sup> indicate the s symmetry or the extended s symmetry of the superconducting OP in the singlet channel. The equations for the temperatures of the instabilities have the standard form

$$1 = -T_{\text{SDW}}^{(\text{r},\text{i})} \sum_{\omega_m} \Gamma_{\text{SDW}}^{(\text{r},\text{i})} \int d\varepsilon_{\mathbf{k}} G_{\mathbf{k}\omega_m}^{\text{h}} G_{\mathbf{k}+\mathbf{Q}\omega_m}^{\text{e}} , \qquad (13)$$

$$1 = -T_{\rm CDW}^{\rm (r,i)} \sum_{\omega_m} \Gamma_{\rm CDW}^{\rm (r,i)} \int d\varepsilon_{\mathbf{k}} G_{\mathbf{k}\omega_m}^{\rm h} G_{\mathbf{k}+\mathbf{Q}\omega_m}^{\rm e} , \qquad (14)$$

$$1 = -T_{\rm SC}^{(\rm s,s^+)} \sum_{\omega_m} \Gamma_{\rm SC}^{(\rm s,s^+)} \int d\varepsilon_{\mathbf{k}} G^{\rm h}_{\mathbf{k}\omega_m} G^{\rm h}_{-\mathbf{k},-\omega_m} , \qquad (15)$$

where  $\Gamma_{SDW}^{(r,i)}$ ,  $\Gamma_{CDW}^{(r,i)}$ ,  $\Gamma_{SC}^{(s)}$ , and  $\Gamma_{SC}^{(s^+)}$  are the total interactions in the SDW, CDW, and SC channels:

$$\Gamma_{\text{SDW}}^{(\text{r,i})} = u_1 \pm u_3 , \qquad \Gamma_{\text{CDW}}^{(\text{r,i})} = u_1 \mp u_3 - 2u_2 , \qquad (16)$$
  
$$\Gamma_{\text{SC}}^{(\text{s})} = u_4 + u_3 , \qquad \Gamma_{\text{SC}}^{(\text{s}^+)} = u_4 - u_3 .$$

The s-type state here means a superconducting state with an isotropic gap on the hole and electron sheets of the FS with the gap  $\Delta$  of the same magnitude and sign. The s<sup>+</sup> state is defined as the superconducting state with gaps that have the same magnitudes but different signs on the corresponding sheets.

In the mean-field approximation, we have

$$\Gamma_{\text{SDW}}^{(r)} \approx u_{11}, \quad \Gamma_{\text{SDW}}^{(i)} \approx u_{12},$$

$$\Gamma_{\text{CDW}}^{(r)} \approx 2u_{12} - u_{11}, \quad \Gamma_{\text{CDW}}^{(i)} \approx u_{12},$$

$$\Gamma_{\text{SC}}^{(s)} \approx u_{11}, \quad \Gamma_{\text{SC}}^{(s^+)} \approx u_{12},$$
(17)

where  $u_{11} = U_{11}N(E_{\rm F})$  and  $u_{12} = U_{12}N(E_{\rm F})$  are the dimensionless intraorbital and interorbital Coulomb interactions, respectively. Hence, in the mean-field approximation,  $\Gamma_{\rm SDW}^{(r)}$  is the largest coupling if  $u_{11} \gtrsim u_{12}$  and  $\Gamma_{\rm CDW}^{(r)}$  is the largest if  $u_{11} \lesssim u_{12}$ , and therefore the system manifests the standard SDW or CDW instability. The SC instability requires an attractive interaction (negative  $\Gamma_{\rm SC}^{(s,s^+)}$ ) and does not manifest itself in the mean-field approximation.

We can go beyond the mean-field approximation by using the renormalization-group approach in the one-loop approximation. The renormalized coupling constants allow attraction in the Cooper channel. In this case, it is necessary to search for both the SDW and SC instabilities, because they can appear simultaneously. This follows because under the condition  $\varepsilon_{\mathbf{k}}^{h} = -\varepsilon_{\mathbf{k}+\mathbf{Q}}^{e}$ , which guarantees an equal number of holes and electrons under the Fermi level in the undoped compound, the SDW and SC susceptibilities diverge logarithmically at low temperatures:

$$-T\sum_{\omega_m} \int d\varepsilon_{\mathbf{k}} G^{\mathbf{h}}_{\mathbf{k}\omega_m} G^{\mathbf{e}}_{\mathbf{k}+\mathbf{Q}\omega_m} = T\sum_{\omega_m} \int d\varepsilon_{\mathbf{k}} G^{\mathbf{h}}_{\mathbf{k}\omega_m} G^{\mathbf{h}}_{-\mathbf{k},-\omega_m}$$
$$= \int_0^{E_{\mathrm{F}}} \tanh\left(\frac{\omega}{2T}\right) \frac{d\omega}{\omega} = \ln\frac{E_{\mathrm{F}}}{T} .$$
(18)

It follows from Eqns (13) and (15) that the instability type is determined by the higher (of two possible) temperatures:

$$T_{\rm SDW}^{\rm (r)} \approx E_{\rm F} \exp\left(-\frac{1}{\Gamma_{\rm SDW}^{\rm (r)}}\right),$$
(19)  
$$T_{\rm SC}^{\rm (s^+)} \sim E_{\rm F} \exp\left(-\frac{1}{\Gamma_{\rm SC}^{\rm (s^+)}}\right).$$

If  $\Gamma_{\text{SDW}}^{(r)}$  is greater than  $\Gamma_{\text{SC}}^{(s^+)}$ , then the SDW instability appears first. In [148], this was assumed to occur in undoped compounds in which an SDW ordering arises. Upon electron doping, the FS expands and the condition  $\varepsilon_{\mathbf{k}}^{\text{h}} = -\varepsilon_{\mathbf{k}+\mathbf{Q}}^{e}$  is violated. In this situation, the logarithmic singularity is cut off and  $T_{\text{SDW}}^{(r)}$  decreases, thereby creating conditions for the appearance of the s<sup>+</sup> instability. With increasing the doping level,  $T_{\text{SC}}^{(s^+)}$  remains almost unaltered, whereas  $T_{\text{SDW}}^{(r)}$ decreases. The above scenario gives only a qualitative structure of the phase diagram on the (T, x) plane and cannot explain the changes in the superconducting transition temperature depending on the level of doping.

The superconducting state with the s<sup>+</sup> symmetry of the OP is isotropic, and the superconducting gap has no zeros on the FS. The line of zeros lies in the Brillouin-zone region between the hole and the electron sheets of the FS. This state has features of the conventional BCS state. In particular, the solution of the nonlinear equation for the gap  $\Delta$  yields the same relation,  $2\Delta = 3.52T_c$ , as for the isotropic s state in the weak-coupling approximation. But the presence of a line of zeros between the FS sheets leads to a specific behavior of a number of the experimentally observed characteristics of substances, which can easily be assumed to be due to the manifestation of zeros of the gap function on the FS in the case of other symmetries of the OP, for example, of the d or p type.

Nevertheless, there is an essential difference between the s and s<sup>+</sup> states if the superconductor contains nonmagnetic impurities. These impurities do not affect the  $T_c$  temperature in the case of the s symmetry of the order parameter, but they affect the s<sup>+</sup> state just like magnetic impurities in the conventional superconductor, i.e., reduce  $T_c$ . For the s<sup>+</sup> state, the impurity potential  $U_{imp}(\mathbf{q})$  contains both the intraband  $(U_{imp}(\mathbf{0}))$  and interband  $(U_{imp}(\mathbf{Q}))$  components. The  $U_{imp}(\mathbf{Q})$  component transfers fermions with  $\Delta$  and  $-\Delta$  gaps, thus acting as a magnetic impurity. This scattering also changes the behavior of the magnetic susceptibility in the superconducting phase.

The dynamic susceptibility in the random-phase approximation (RPA) is given by the standard formula

$$\chi_{\rm s}(\mathbf{q},\Omega) = \frac{\chi_{\rm s}^0(\mathbf{q},\Omega)}{1 - \Gamma_{\rm SDW}^{(\rm r)} \chi_{\rm s}^0(\mathbf{q},\Omega)} \,, \tag{20}$$

where  $\Omega$  is the frequency of the boson spectrum. The quantity  $\chi_s^0(\mathbf{q}, \Omega)$  for the s<sup>+</sup> superconductor in the 'clean' limit (without impurities) for  $\mathbf{q} \approx \mathbf{Q}$  has the asymptotic



**Figure 18.** Calculated temperature dependences of  $1/T_1$  for superconductors of the s<sup>+</sup> type with nonmagnetic impurities in comparison with NMR data: (a) [148] and (b) [147].

behavior

$$\frac{\operatorname{Im}\chi_{s}^{0}(\mathbf{q},\Omega)}{\Omega}\Big|_{\Omega\to0}\sim\left(\mathbf{q}-\mathbf{Q}\right)^{2},\tag{21}$$

and is therefore small. This smallness leads to an exponential smallness of the inverse relaxation time  $1/T_1$  measured in NMR experiments, in view of the known relation

$$\frac{1}{T_{1}} \sim T \sum_{\mathbf{q}} \frac{\mathrm{Im}\,\chi_{s}(\mathbf{q},\Omega)}{\Omega} \bigg|_{\Omega=0} \\ \sim T \sum_{\mathbf{q}} \chi_{s}^{2}(\mathbf{q},0) \bigg[ \frac{\mathrm{Im}\,\chi_{s}^{0}(\mathbf{q},\Omega)}{\Omega} \bigg]_{\Omega=0}.$$
(22)

Because  $\chi_s(\mathbf{q}, 0)$  has a maximum in the vicinity of  $\mathbf{q} = \mathbf{Q}$ , the relaxation rate  $1/T_1$  is small by virtue of asymptotic behavior (21). But in the presence of nonmagnetic impurities,  $1/T_1$  in (22) is no longer exponentially small. A numerical calculation shows that it actually increases with temperature in accordance with a power law. The exponent in the relation  $1/T_1 \sim T^{\alpha}$  decreases with increasing the parameter  $b = 2U_{imp}(\pi)/\Delta$ , i.e., the strength of scattering of a fermion from sheet to sheet of the FS. The numerical results for  $1/T_1$ , together with experimental data, are presented in Fig. 18a. At low temperatures,  $1/T_1$  is exponentially small, but in the range of intermediate temperatures  $(T \leq T_c)$ , it varies approximately with a power law, with  $\alpha = 2-3$ . For superconductors with a d symmetry of the order parameter, we have  $1/T_1 \sim T^3$  because of the presence of a line of zeros on the FS. The power-law behavior of  $1/T_1$  observed in NMR experiments in FeAs systems was interpreted as evidence of the existence of zeros in the gap on the FS. But as shown in [148], such a behavior can be caused by the presence of impurities in a superconductor of the s<sup>+</sup> type, where there are two different-sign gaps on two sheets of the FS.

Figure 18b displays analogous results of the computation of  $1/T_1$  for an s<sup>+</sup> superconductor with nonmagnetic impurities [147]. The calculations in [147, 148] were performed simultaneously and independently. On the basis of natural assumptions on the parameters of the Hamiltonian consistent with LDA calculations of the electronic structure of FeAs compounds, the minimal model described in this section allows finding the solution of the equations for a superconductor with two different-sign gaps on the hole and electron sheets of the FS and giving a new interpretation of experimental results concerning measurements of nuclear relaxation in a number of compounds.

Simultaneously with [147, 148], paper [153] appeared in which the same minimal model was used with the interaction between the holes and electrons via antiferromagnetic fluctuations with  $\mathbf{q} \approx \mathbf{Q}$ . The solution of the equations for the superconducting gap that were written in the mean-field approximation shows that the s<sup>+</sup> state is energetically more favorable than the state with another symmetry. Together with solutions for the s and s<sup>+</sup> states, solutions that were called 'double d-wave gap states' were obtained in [153]; these are states in which a superconducting gap with a d symmetry is realized on both the hole and the electron sheet, but the gaps are in antiphase to each other.

We also mention Ref. [154], where instead of the itinerantelectron model, the authors used a Heisenberg model with two exchange interactions  $J_1$  and  $J_2$  between Fe atoms in the FeAs<sub>4</sub> plane, which additionally takes electron hopping over the lattice into account (the so-called  $t-J_1-J_2$  model [151]). It was shown that two types of the d symmetry of the OP,

$$d_{x^2-y^2} :\sim \Delta_0(\cos k_x - \cos k_y),$$
  
$$d_{xy} :\sim \Delta_0 \sin k_x \sin k_y,$$

and three types of the s symmetry,

$$s_0: \sim \Delta_0, \qquad s_{x^2+y^2}: \sim \Delta_0(\cos k_x + \cos k_y),$$
  
$$s_{x^2y^2}: \sim \Delta_0 \cos k_x \cos k_y,$$

are possible in this model.

The spectrum of noninteracting electrons has the hole and electron FSs spaced by the vector **Q**; the superconducting OP with the  $s_{x^2y^2}$  symmetry reverses its sign on these sheets similarly to how this occurs in the s<sup>+</sup> state considered above. For the  $s_{x^2y^2}$  state, the tunnel differential conductance dI/dV, the penetration depth  $\lambda(T)$ , and the spin– lattice relaxation rate  $1/T_1$  have been calculated; it has also been shown how these quantities are affected by the zeros of the superconducting gap that lie between the hole and electron sheets of the FS.

The above-described minimal model was recently extended with the purpose of reaching a better correspondence with real La<sub>1-x</sub>O<sub>y</sub>FeAs compounds [155]. Taking into account that the unit cell contains two Fe atoms, the authors

of Ref. [155] considered five 3d orbitals  $(d_{3z^2-r^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, and d_{zx})$  for each of the two Fe atoms, and three 4p orbitals  $(p_x, p_y, p_z)$  for each of the two As atoms. As a result, the basis of the electron states of the model includes 16 orbitals; the Hamiltonian of the resultant p-d model was written in the tight-binding approximation. The Hamiltonian included the local Coulomb interactions of Fe atoms U (intraorbital) and U' (interorbital), and the Hund parameter J and the pair-transfer parameter J'. These parameters of the tight-binding Hamiltonian were chosen using the procedure of fitting the calculated electronic structure to the structure calculated in the LDA for a specific compound with two hole FSs near the  $\Gamma$  point and two electron FSs near the M point.

With the aid of the thus constructed Hamiltonian of the p-d model, a matrix of magnetic interactions was calculated in the RPA; the matrix reveals a peak around the  $\Gamma$  point, which occurs as a result of nesting between two hole pockets of the FSs and between two electron pockets. A stronger peak at the M point appears due to the nesting between the electron and hole pockets separated by the vector **Q**. The calculated dynamic susceptibility determines the kernels of the Eliashberg integral equations for the superconductor.

A numerical solution of these equations with the parameters U = 1.5 eV, U' = 1.0 eV, J = J' = 0.25 eV, x = 0.1, and T = 0.002 eV yields the maximum magnitude of  $T_c$ corresponding to the s<sup>+</sup> symmetry. On the other hand, at U = 1.68 eV, U' = 1.4 eV, J = J' = 0.14 eV, x = 0.1, and T = 0.002 eV, the magnitude of  $T_c$  corresponds to the  $d_{xy}$  symmetry with zeros of the gap on the FS. An analysis shows that the selection between these two states is determined by the parameter J/U'. At large J/U', the most probable event is the appearance of the s<sup>+</sup> symmetry, in which case the gap reverses sign between the hole and electron pockets of the FS. At smaller J/U', the  $d_{xy}$  symmetry with zeros on the FS is energetically advantageous.

#### 5.4 Derivation of the effective Hamiltonian

The minimal model of the FeAs systems described in Section 5.2 is, in essence, a phenomenological model with indeterminate parameters of the Hamiltonian. It is interesting, to derive this model based on the complete atomic electron structure of a compound (for example, LaOFeAs) and first-principle numerical calculations. This program has to a certain extent been realized in paper [156], whose authors proceeded from the atomic approximation of the compound, taking into account that it is formed by alternating planes consisting of FeAs<sub>4</sub> complexes separated by LaO layers.

The comparison of the results of an LDA calculation of the three-dimensional compound LaOFeAs with the results of calculations of a single FeAs plane shows that in the region of energies close to the Fermi level, the difference in the band structure is very small because of the smallness of the interplanar interaction of 3d states of Fe through LaO layers. Therefore, the truncated model of the compound describing a single FeAs plane adequately describes the physical properties of the complete compound.

An FeAs plane in fact consists of three planes; one of these is a square lattice of Fe atoms, and the other two (arranged above and below it) are lattices of As atoms, such that each Fe atom is surrounded by an octahedron of As atoms. The d states of Fe form five orbitals:  $(d_{xz}, d_{yz})$ ,  $(d_{xy}, d_{z^2})$ , and  $d_{x^2-y^2}$ . These orbitals, which are degenerate in a free atom, undergo an orbital splitting in the crystal field of distorted

(24)



**Figure 19.** Structure of occupied states in Fe and As atoms of a single FeAs plane in the undoped LaOFeAs compound [156].

octahedra. The s and p states of As atoms are partially hybridized and form a basis consisting of four states:  $p_x$ ,  $p_y$ ,  $sp_z^+$ , and  $sp_z^-$ , where  $sp_z^\pm = a|s\rangle \pm b|p_z\rangle$  (Fig. 19). In the undoped compound, the Fe<sup>2+</sup> and As<sup>3-</sup> ions contain 14 electrons, which are distributed over the orbitals as shown in Fig. 19.

The Hamiltonian of a single FeAs plane in the tightbinding approximation is written as a sum of three terms,  $H = H_a + T + U$ , where

$$H_{\rm a} = \sum_{i\nu\sigma} \varepsilon_{\rm d}(\nu) d_{i\sigma}^{\nu+} d_{i\sigma}^{\nu} + \sum_{l\alpha\sigma} \varepsilon_{\rm sp}(\alpha) s p_{l\sigma}^{\alpha+} s p_{l\sigma}^{\alpha} , \qquad (23)$$

$$T = -\sum_{\langle ij\rangle\sigma\nu\nu'} (t_{\nu\nu'}d_{j\sigma}^{\nu'+}d_{i\sigma}^{\nu} + \text{h.c.}) - \sum_{i\sigma\nu\alpha}\sum_{l(i)} (V_{il}^{\nu\alpha}d_{i\sigma}^{\nu+}sp_{l\sigma}^{\alpha} + \text{h.c.}),$$

$$U = \sum_{\nu} U_{\nu}^{d} \sum_{i} n_{di\uparrow}^{\nu} n_{di\downarrow}^{\nu} + \sum_{\nu} U_{\nu}^{\text{sp}} \sum_{i} n_{\text{spi}\uparrow}^{\nu} n_{\text{spi}\downarrow}^{\nu}$$
$$- \sum_{\nu\nu'} J_{\nu\nu'}^{H} \sum_{i} \mathbf{S}_{di}^{\nu} \mathbf{S}_{di'}^{\nu'}.$$
(25)

Here, the subscript *i* labels the sites occupied by Fe atoms; v = 1, ..., 5 are the order labels of the d orbitals; *l* is the order number of an As atom; and the superscript  $\alpha = 1, ..., 4$  labels the hybridized sp orbitals. The individual terms in *H* have the following interpretation:  $H_0$  is the energy of atomic levels on the Fe and As lattices and *T* is the operator of the transition of a d electron from a site to an adjacent site and of the hybridization of d and sp electrons at adjacent sites. Term (25) describes the Coulomb repulsion of electrons on d and sp orbitals and the Hund intra-atomic electron transfer between all d orbitals.

To determine numerical values of the hopping and hybridization parameters entering Eqns (23) and (24), the authors fit the electron spectrum of the FeAs layer calculated by the LDA method to that obtained by diagonalizing the Hamiltonian in (23) and (24). The tables of the values obtained are given in Ref. [156]. It follows from these tables that the energies of  $\varepsilon_d(v)$  and  $\varepsilon_{sp}(\alpha)$  are near -4.8 eV and differ only a little for different d orbitals (by less than 1 eV). On the other hand, the hopping and hybridization matrix elements are very small (if they are not equal to zero by the symmetry condition), i.e., less than 1 eV.

The Coulomb energy in FeAs compounds is of the order of 5 eV, which substantially exceeds the values of the matrix elements of the hopping and hybridization parameters; therefore, it is possible to derive the effective Hamiltonian using the perturbation theory near the atomic limit. It is convenient to represent it in the form

$$H_{\rm eff} = H_{xz,yz} + H_{xy,z^2} + H_{x^2 - y^2, x^2 - y^2} - J^{\rm H} \sum_{i\mu\mu'} \mathbf{S}_i^{\mu} \mathbf{S}_i^{\mu'}.$$
 (26)

The first three terms can be written in the form of a single expression

$$H_{\mu\mu'} = -\sum_{\langle ij \rangle \nu\nu'\sigma} \tilde{t}_{\nu\nu'} c^{+}_{j\nu'\sigma} c_{i\nu\sigma} - \sum_{\langle \langle ij \rangle \rangle \sigma\nu} \tilde{t}'_{\nu\nu} c^{+}_{j\nu\sigma} c_{i\nu\sigma} + \sum_{\langle \langle ij \rangle \rangle \nu\nu'} J_{\nu\nu'} \mathbf{S}^{\nu}_{i} \mathbf{S}^{\nu'}_{j} + \sum_{\langle \langle ij \rangle \rangle \nu} J'_{\nu\nu} \mathbf{S}^{\nu}_{i} \mathbf{S}^{\nu}_{j}.$$
(27)

The summation over v and v' in (27) ranges all orbitals grouped into three blocks [see the subscripts in the separate terms in Hamiltonian (26)]. These blocks are independent of one another. But the Hund term in Hamiltonian (26) links them between themselves.

Thus, the complete set of five orbitals is divided into three sectors: (xz, yz),  $(xy, z^2)$ , and  $(z^2 - y^2, z^2 - y^2)$ . In each block, the Hamiltonian describes electron motion over the lattice that belongs to the related orbitals with an effective exchange interaction between the nearest and next-to-nearest Fe atoms. The common Hund term, which describes the intra-atomic exchange between the electrons that belong to all orbitals, serves to couple the subsystems (blocks).

Each of the three  $H_{\mu\mu'}$  corresponds in its structure to the tJ model, which is the limit case of the strong Coulomb interaction. As in the tJ model, the exchange parameters arise in the second-order perturbation theory in hopping and in the fourth order in hybridization:

$$J_{\nu\nu'} \approx 4 \, \frac{t_{\nu\nu'}^2}{U^{\rm d}}, \qquad J_{\nu\nu'}' \approx 4 \, \frac{V_{\nu}^4}{(U^{\rm d})^3} \,.$$
 (28)

These exchange interactions are antiferromagnetic, whereas the Hund intra-atomic exchange is ferromagnetic. Hence, between the nearest neighbors in the effective FeAs layer, there are frustrating antiferromagnetic interactions and the Hund interaction, which tends to organize a ferromagnetic order due to electron motion over the lattice.

An analysis shows that the sector of states that describes the  $d_{xz}$  and  $d_{yz}$  orbitals best corresponds to the properties of the undoped compound LaOFeAs. The AFM structure realized in it (see Fig. 5), consisting of ferromagnetic chains running along one of the basal-plane axes and of chains with an antiferromagnetic alternation of spins in the other two directions, is in agreement with its electronic structure and must be described by the contribution  $H_{xz,yz}$  to effective Hamiltonian (26). The fact that the spins of Fe atoms are aligned ferromagnetically along one direction provides the possibility of electron motion in this direction. This explains why the undoped compounds of the FeAs group, unlike cuprates, are metals rather than insulators.

We note one more paper [157], in which the effective Hamiltonian is also derived based on the minimal two-band model in the tight-binding approximation. The starting Hamiltonian is taken in the form  $H = H_0 + H_{int}$ , where

$$H_{0} = \sum_{\mathbf{k}nn\sigma} (\varepsilon_{\mathbf{k}}^{nm} - \mu) c_{\mathbf{k}n\sigma}^{+} c_{\mathbf{k}n\sigma} , \qquad (29)$$
$$H_{\text{int}} = \sum (Un_{\text{int}} n_{\text{int}} + Jc_{-s}^{+} c_{-s}^{+} c_{-s}^{+} c_{\text{int}})$$

$$+ \sum_{i\sigma\sigma'} (U_{12}n_{i1\sigma}n_{i2\sigma'} + Jc^+_{i1\sigma}c^+_{i2\sigma'}c_{i1\sigma'}c_{i2\sigma}).$$
(30)

Here, n, m = 1, 2 label the orbitals  $d_{xz}$  and  $d_{yz}$ .

The Hamiltonian  $H_{int}$  allows both the on-site Coulomb repulsion of electrons that are in the same or in different orbitals, and the Hund exchange and pair transfer with the same parameter J.

In the tight-binding approximation  $(U, U_{12}, J \ge t)$ , the effective Hamiltonian is derived in the second-order approximation in hopping (in the spirit of the tJ model); its parameters are selected so as to have the FS consisting of two hole pockets [at the points  $\Gamma(0,0)$  and  $M(\pi,\pi)$ ] and two electron pockets [at the points  $X(\pi, 0)$  and  $Y(0, \pi)$ ]. The authors of Ref. [157] rely on the results of numerical calculations of the compound LaOFeAs [61, 138]. Such a model reveals an attraction between the electrons located on the same sheet of the FS or between the holes. The interaction of electrons with holes (located on different sheets) leads to one of two states: with the  $s^+$  or d symmetry of the OP. The state of the extended s<sup>+</sup> symmetry (with the change of sign or on different sheets) is more stable than the d state in a wide range of the parameters. The d symmetry of the OP is energetically advantageous at large J. This last conclusion contradicts the results in Ref. [155], whose authors used the extended model with all five d orbitals taken into account.

Certainly, the results of the analysis of the superconducting OP in FeAs systems can differ depending on the chosen parameters of the Hamiltonian and on the number of orbitals considered, but the possibility of a specific s<sup>+</sup> symmetry of the OP finds increasingly greater confirmation in theoretical works.

#### 5.5 Role of electron correlations

The energy-band structure of all FeAs systems was calculated in the LDA, which ignores electron correlations. But the nature of the FS agrees with the experimental data sufficiently well; this gives grounds to assume that FeAs systems are weakly correlated systems. At the same time, some experimental facts, such as the high electric resistance ('poor' metallic properties) in the normal state [158], the absence of a Drude peak in the optical conductivity [158], and a strong temperature-dependent transfer of the spectral weight in optical measurements [159], support the existence of strong correlations.

The question of whether FeAs systems are weakly or strongly correlated materials therefore remains open. In this situation, it is important to have calculations of the electronic structure with the correlation effects taken into account for specific compounds in the framework of the LDA+DMFT method based on the dynamical mean-field theory (DMFT).

In Ref. [13], the band structure of LaOFeAs was calculated by the LDA + DMFT method using the high-accuracy Monte Carlo technique with continuous time to solve the auxiliary single-impurity problem. The following values of the interaction parameters were taken: the on-site Coulomb repulsion of d electrons U = 4 eV and the Hund exchange integral J = 0.7 eV. The dispersion curve and the



**Figure 20.** Comparison of the theoretical and experimental densities of 3d states of Fe in LaOFeAs: (a) the partial density of 3d and 4p states of Fe and As atoms, respectively, in the LaOFeAs compound calculated using the LDA+DMFT method in comparison with the results of LDA calculations [13]; and (b) the density of 3d states according to the data of resonant X-ray emission spectroscopy (RXES) [160].

total and partial densities of states were calculated at the fixed temperature T = 116 K. We give only the data on the partial density of 3d states of Fe and 4d states of As (Fig. 20a).

As can be seen from this figure, the electron correlations with the parameters U = 4 eV and J = 0.7 eV result in a radical rearrangement of the spectrum compared to that obtained in LDA calculations. The 3d band, which initially occupied the energy range from -2 to 2 eV, is substantially extended; far from the Fermi level, lower and upper Hubbard bands are formed. In the vicinity of the Fermi level, the quasiparticle peak strongly decreases; its intensity is  $Z \approx 0.2 - 0.3$ . Therefore, with the parameters chosen, the system is strongly correlated. As the parameter U increases to 4.5 eV, a gap on the FS appears, which indicates that LaOFeAs is in a state close to the Mott-Hubbard phase transition into the insulator state. This conclusion contradicts experimental data, in particular, the results of resonance Xray emission spectroscopy (Fig. 20b), which gives a distribution close to that obtained in LDA calculations [160].

The authors of [161], who used the LDA+DMFT approach with the same values of the parameters U and J, come to the conclusion that LaOFeAs is a rather weakly correlated material. In particular, as U increases to 5 eV, the system remains metallic; in other words, LaOFeAs is far from the Mott-Hubbard transition. Both works [13, 161] seem to indicate that this system remains moderately correlated, and

the divergence of the quantitative results is related to a difference in the computational procedures.

The problem of correlations was also studied in detail in Ref. [162]. The authors of [162] calculated (in the RPA) the effective Coulomb potentials of the atoms of Fe and rareearth elements in *RE*OFeAs compounds (RE = Ce, Nd, Pr) that occur as a result of screening by the electrons of other orbitals. It turned out that the magnitude of U is substantially greater in these compounds than in elemental metals Fe and Ce. In particular, in Fe atoms, the potential U proved to be equal to 3.69 eV. This value is of the same order as that used in the calculations in Refs [13, 161] (U = 4 eV), but is nevertheless smaller. An increase in the Coulomb interaction in compounds in comparison with the Coulomb interaction in pure metals is apparently related to their layered structure, which results in that the other electrons of the compound screen the bare Coulomb potentials insufficiently [162]. The value of U for 4f electrons in Ce atoms proved to be equal to 9 eV.

The authors of Ref. [162] also investigated correlation effects on the 4f states of rare-earth atoms *RE* in *RE*OFeAs compounds using the LDA+DMFT method. It turned out that in compounds with Pr and Nd, the occupied 4f bands were located deep below the Fermi level and manifested themselves in localized magnetic moments weakly coupled to 3d electrons at the Fermi level. But in CeOFeAs, the occupied 4f states lie immediately below the 3d band, which can lead to the Kondo screening of their moments. Under the effect of pressure, a competition between the formation of Kondo singlets in Ce atoms and Cooper pairing can occur (in other words, the competition between heavy fermions and superconductivity). However, this idea needs experimental verification.

Certainly, electron correlations should play some role in FeAs systems, but to what class these compounds should be referred — moderately correlated or weakly correlated — is still not clear.<sup>1</sup>

#### 6. Conclusion

In the half year that passed from the moment of the discovery of a new class of high-temperature superconductors, the FeAs compounds, the efforts of the world community of physicists, chemists, and technologists ensured great progress in explaining their nature. The related activity of researchers is compared only with that observed after the discovery of high-temperature superconductivity in cuprates. However, the present period of studies differs significantly from that situation. Twenty years ago, researchers worked, as they were, in the twilight, whereas now they have enormous experience in handling complex compounds, the newest experimental techniques, perfect computer technology, and, most importantly, numerous physical ideas developed in studying the cuprates, which were immediately used for studying the new HTSC materials.

The instantaneous propagation of information through electronic data files and data bases contributed much to the unprecedentedly rapid advance of studies of FeAs compounds. Deserving special attention is the international nature of the collaboration; as a rule, papers concerning FeAs systems are published by groups of authors from several different countries and laboratories, comprising specialists of different profiles. All this favors a very rapid accumulation of information about the properties of the objects investigated and leads to deep insights into the experimental material. In the half year that passed from the moment of the discovery of this new class of HTSCs, about five hundred works were published, which means that two to three new works appeared daily in the electronic archives.

When studying the cuprate HTSCs, many years of experiments were needed for understanding these materials; in the case of FeAs compounds, a half of a year of studies proved to be sufficient for explaining the physical bases of this new class of compounds, and now time has already come for generalizing the results. This review is an attempt aimed at such a systematic generalization. So, what do we definitely know about the physical properties of FeAs systems?

First, we know their crystallochemical and electronic structures. The different classes of compounds pertaining to FeAs systems, such as *RE*OFeAs,  $AFe_2As_2$ , LiFeAs, are all layered structures consisting of alternating FeAs layers built from FeAs<sub>4</sub> complexes. These layers are the main structural element that determines the electron properties of these compounds. As a result of the layered structure, FeAs compounds are quasi-two-dimensional as regards their electronic properties. This relates them to cuprates built from alternating CuO<sub>2</sub> planes, in which the electronic properties are mainly determined by the electron orbitals of the atoms of these layers and only to a lesser extent by the orbitals of atoms that are located between these layers.

But there is an essential difference between FeAs systems and the cuprates, which lies in the fact that the initial (stoichiometric) compounds are insulators in the case of cuprates and metals in FeAs systems. In both cases, however, the initial compounds are antiferromagnetic, although with localized magnetic moments in the first case and with itinerant-electron magnetism in the second. Upon doping the initial compounds, the temperatures of magnetic ordering  $T_N$  decrease sharply and the compounds become superconducting at concentrations of a dopant of the order of 10% (or even less).

In both classes of these HTSC materials, the doping leads to substitution for the atoms that lie outside the main layers of the compounds, i.e., outside the FeAs and CuO<sub>2</sub> layers. The doping creates charge carriers in the main layers, which determine the interesting physics in both classes of HTSC materials. In the new class of HTSCs, as in the cuprates, the doping can create either electrons or holes in the main layer. In FeAs systems, the possibilities of doping are richer because of an easy interchangeability of chemical elements in them. Thus, in *RE*OFeAs compounds, there is a possibility of

<sup>&</sup>lt;sup>1</sup> The study of the role of electron correlations in the REOFeAs compound was recently continued in [163-165]. In earlier works, contradictory results were obtained using the dynamical mean-field theory method (LDA+DMFT). According to Ref. [13], these compounds are strongly correlated and are near the Mott transition, whereas the authors of Ref. [161], who used the same interaction parameters, obtained results that indicate the development of weak correlations. In [163-165], contradictory results were obtained again. Indications of strong correlations were obtained in [163, 164], but convincing proofs that FeAs compounds are weakly correlated systems were found in [165]. These new arguments appeared after the authors of [165] showed the importance of taking the hybridization of the Fe 3d and As 4p states into account, which leads to a spectral density of electron states devoid of typical features of strongly correlated systems; no Hubbard bands and no Kondo peak at the Fermi level are present in the electron spectrum. These results agree well with the data of X-ray and photoemission spectroscopy. Thus, increasingly more data appear that indicate that FeAs compounds are systems with weak or at most moderate electron correlations.

substituting for a rare-earth element (for example, with strontium), oxygen (for example, with fluorine), or arsenic (for example, with phosphorus). Depending on the relation between the valences of the ion to be substituted and the dopant, either electrons or holes appear in the FeAs layers. It is remarkable that there can occur a partial substitution for the atoms of the main layer, e.g., for Fe atoms with Co atoms; in this case, superconductivity is induced in the doped compound, in contrast to cuprates, where the substitution for Cu atoms located in the main layer destroys superconductivity.

Phase diagrams on the (T, x) plane, where x is the concentration of the dopant, are very similar. Nevertheless, there is an essential difference between the cuprates and FeAs systems caused by electron correlations. Doped HTSC cuprates, in contrast to FeAs systems, are near the Mott– Hubbard metal–insulator transition, although in both cases superconductivity appears near the transition to the anti-ferromagnetic state. This means that the cuprates belong to materials with strong electron correlations, whereas FeAs systems are weakly (or moderately) correlated materials, although this question is still not clear.

Another question that has been thoroughly studied is that of the electronic structure of FeAs compounds. In spite of the different crystal structure of compounds of the REOFeAs, AFe<sub>2</sub>As<sub>2</sub>, and LiFeAs types, all of them have a similar electronic structure caused by the existence of a common structural element, the FeAs planes. With all the differences in chemical composition, their electronic structure remains unaltered on the whole. Electron states near the Fermi level are formed by 3d orbitals of Fe hybridized with 4p orbitals of As. The density of states at the Fermi level in these systems is higher than in the cuprates, although the charge carrier density is lower. The FS calculated from first principles in the local density approximation is multisheeted. It has two cylindrical sheets (as a result of the two-dimensional nature of electron states) in the center of the Brillouin zone, which correspond to holes, and two sheets in its corners, which correspond to electrons. The same structure of the FS is characteristic of undoped compounds; the doping only changes the sizes of the electron and hole pockets. The  $\Gamma$ and M points around which the hole and electron pockets are located are separated by the vector  $\mathbf{Q} = (\pi, \pi)$ , which connects both types of pockets. This nesting causes an antiferromagnetic order of the SDW type with the wave vector Q in all FeAs compounds; moreover, the antiferromagnetic structure is common to all FeAs compounds. We emphasize that in spite of the large number of versions of the chemical composition of FeAs compounds (within the same crystal structure), their electronic and magnetic structures remain the same.

The proximity to antiferromagnetic ordering in cuprates and in FeAs systems causes, apparently, the spin-fluctuation mechanism of pairing, which leads to high values of  $T_c$  in both cases. We note that in the case of the cuprates, this idea is confirmed by the d symmetry of the superconducting order parameter, which was reliably established experimentally, whereas in FeAs systems, this is the subject of the most urgent experiments to date. Different experimental techniques give contradictory results concerning the symmetry of the superconducting order parameter in the new HTSCs. Some studies show the s symmetry of the OP, whereas others demonstrate signs of the existence of a line of zeros of the OP on the FS, in particular, in experiments on the measurement of the spin-lattice relaxation rate  $1/T_1$  by the NMR method. However, there is the interesting concept of the existence in the FeAs systems of a specific s<sup>+</sup> symmetry of the superconducting OP, upon which a nodeless gap is realized on the hole and electron sheets of the FS with the standard s symmetry, but with different signs on the different sheets. This means that the superconducting OP as a function of the momentum in the entire Brillouin zone passes through zero somewhere outside the hole and electron pockets. In this case, in the presence of a nonmagnetic impurity, there must be a power-law dependence of  $1/T_1$  on temperature, which can ensure an alternative explanation of the power-law dependence of  $1/T_1$  observed in NMR experiments, which was interpreted in favor of the d or p symmetry of the OP. The clarification of the type of symmetry of the superconducting OP in FeAs superconductors is the primary task, which must be solved in order to understand the mechanism of pairing. Although progress in the synthesis of single crystals of compounds in recent years has brought the solution to this problem significantly closer, the number of questions still exceeds the number of answers.

We see how rapidly the synthesis of new compounds has developed in the last few years. There was discovered a new class of layered systems (FeSe, FeS, FeTe) that do not contain As, but nevertheless have the same structural element FeSe<sub>4</sub> (similar to FeAs<sub>4</sub>) forming the principal planes. In this new class of layered systems, superconductivity with a sufficiently high  $T_c$  (27 K in FeSe) can arise under the action of pressure. The fact important for the understanding of the superconductivity mechanism in all FeAs systems is that all these compounds are antiferromagnets in the stoichiometric composition. There is no doubt that new types of superconducting compounds will be discovered in FeAs systems.

The discovery of a new class of HTSCs in FeAs systems allows expecting the appearance of new HTSC systems among chemical compounds. A guiding thread for physicists searching for new systems is the idea of the potential of transition-element-based layered structures, which are antiferromagnets in the stoichiometric composition and which easily allow substitutions for some of the composing chemical elements. For chemists, the most important ideas are those related to the crystal chemistry and the analysis of the valence of the ions in the synthesized compounds. However, completely unexpected discoveries are possible in this field.

This work was supported in part by the Council of the President of the Russian Federation for Leading Scientific Schools (project nos. LSS-1941.2008.2 and LSS-1929.2008.2).

#### References

- 1. Kamihara Y et al. J. Am. Chem. Soc. 128 10012 (2006)
- 2. Watanabe T et al. Inorg. Chem. 46 7719 (2007)
- 3. Kamihara Y et al. J. Am. Chem. Soc. 130 3296 (2008)
- 4. Chen G F et al. Phys. Rev. Lett. 100 247002 (2008)
- 5. Ren Z-A et al. Mater. Res. Innovat. 12 (3) 56 (2008)
- 6. Ren Z-A et al. Chinese Phys. Lett. 25 2215 (2008)
- 7. Margadonna S et al. Phys. Rev. B 79 014503 (2009)
- 8. Rotter M, Tegel M, Johrendt D Phys. Rev. Lett. 101 107006 (2008)
- 9. Tapp J H et al. *Phys. Rev. B* 78 060505(R) (2008)
- 10. Wang X C et al. Solid State Commun. 148 538 (2008)
- 11. Mizuguchi Y et al. *Appl. Phys. Lett.* **93** 152505 (2008)
- 12. Boeri L, Dolgov O V, Golubov A A Phys. Rev. Lett. 101 026403 (2008)
- 13. Haule K, Shim J H, Kotliar G Phys. Rev. Lett. 100 226402 (2008)
- 14. Yang J et al., arXiv:0809.3582
- 15. Lu W et al. Solid State Commun. 148 168 (2008)

114.

115.

116.

118

119

120.

121.

122.

123.

124.

125.

126.

128.

129

130.

131.

132.

133.

134.

135.

136.

137.

138.

143.

144.

145.

146.

147.

148

149

150

151.

152.

153.

154.

155

156.

157.

159

160.

161.

162

163.

164.

(2008)

arXiv:0805.2958

arXiv:0807.4572

(1)(2009)]

- 16. Ren Z-A et al. Europhys. Lett. 82 57002 (2008) 17.
- Yang J et al. Supercond. Sci. Technol. 21 082001 (2008) Yang H et al., arXiv:0803.0623 18.
- 19 Zhu X et al. Supercond. Sci. Technol. 21 105001 (2008)
- Sefat A S et al. Phys. Rev. B 77 174503 (2008) 20.
- Cheng P et al. Phys. Rev. B 78 134508 (2008) 21
- 22 Mukuda H et al. J. Phys. Soc. Jpn. 77 093704 (2008)
- 23 Wang C et al. Europhys. Lett. 83 67006 (2008)
- Wen H-H et al. Europhys. Lett. 82 17009 (2008) 24.
- 25. Mu G et al., arXiv:0806.2104

1286

- Sefat A S et al. Phys. Rev. B 78 104505 (2008) 26.
- 27 Cao G et al., arXiv:0807.1304
- 28 Li Y K et al., arXiv:0808.3254
- Kawabata A et al., arXiv:0807.3480 29
- Li H et al., arXiv:0807.3153 30.
- Werthamer N R, Helfand E, Hohenberg P C Phys. Rev. 147 295 31. (1966)
- 32 Xu G et al. Europhys. Lett. 82 67002 (2008)
- 33. Wang X L et al., arXiv:0806.0063
- Jia Y et al. Appl. Phys. Lett. 93 032503 (2008) 34.
- 35. Ding L et al. Phys. Rev. B 77 180510(R) (2008)
- Ma Y et al., arXiv:0806.2839 36.
- 37. de la Cruz C et al. Nature 453 899 (2008)
- 38 Dong J et al. Europhys. Lett. 83 27006 (2008)
- Chen Y et al. Phys. Rev. B 78 064515 (2008) 39
- 40. Cao C, Hirschfeld P J, Cheng H-P Phys. Rev. B 77 220506(R) (2008)
- Ma F, Lu Z-Y Phys. Rev. B 78 033111 (2008) 41.
- Zhao J et al. Nature Mater. 7 953 (2008); arXiv:0806.2528 42
- 43 Cimberle R et al., arXiv:0807.1688
- Klauss H-H et al. Phys. Rev. Lett. 101 077005 (2008) 44
- 45. Opahle I et al. Phys. Rev. B 79 024509 (2009)
- 46. Drew A J et al., arXiv:0807.4876
- 47. Lebèque S Phys. Rev. B 75 035110 (2007)
- Singh D J, Du M-H Phys. Rev. Lett. 100 237003 (2008) 48
- 49 Mazin I I et al., arXiv:0806.1869
- 50 Kuroki K et al. Phys. Rev. Lett. 101 087004 (2008)
- Nekrasov I A, Pchelkina Z V, Sadovskii M V Pis'ma Zh. Eksp. Teor. 51. Fiz. 87 647 (2008) [JETP Lett. 87 560 (2008)]
- Vildosola V et al. Phys. Rev. B 78 064518 (2008) 52
- 53. Liu C et al., arXiv:0806.2147
- 54. Lu D H et al. Nature 455 81 (2008)
- 55. Coldea A I et al. Phys. Rev. Lett. 101 216402 (2008)
- 56. Mazin I I et al. Phys. Rev. B 78 085104 (2008)
- Mazin I I et al. Phys. Rev. Lett. 101 057003 (2008) 57.
- 58. Ishibashi S, Terakura K, Hosono H J. Phys. Soc. Jpn. 77 053709 (2008)
- 59 Mazin I I et al., arXiv:0803.2740
- Dai X et al. Phys. Rev. Lett. 101 057008 (2008) 60.
- Lee P A, Wen X-G, arXiv:0804.1739 61.
- Yao Z-J, Li J-X, Wang Z D, arXiv:0804.4166 62
- 63. Wang F et al. Phys. Rev. Lett. 102 047005 (2009)
- 64. Gonnelli R S et al., arXiv:0807.3149
- Grafe H-J et al. Phys. Rev. Lett. 101 047003 (2008) 65.
- Shan L et al. Europhys. Lett. 83 57004 (2008) 66.
- Chen T Y et al. Nature 453 1224 (2008) 67.
- 68. Millo O et al. Phys. Rev. B 78 092505 (2008)
- 69.
- Wang Y-L et al. Supercond. Sci. Technol. 22 015018 (2009) 70
- Samuely P et al. Supercond. Sci. Technol. 22 014003 (2009)
- 71. Martin C et al., arXiv:0807.0876
- Kondo T et al. Phys. Rev. Lett. 101 147003 (2008) 72.
- 73 Pan M H et al., arXiv:0808.0895
- 74. Aiura Y et al. J. Phys. Soc. Jpn. 77 103712 (2008); arXiv:0808.1063
- 75 Matano K et al. Europhys. Lett. 83 57001 (2008)
- Luetkens H et al. Phys. Rev. Lett. 101 097009 (2008) 76.
- 77. Yates K A et al. Supercond. Sci. Technol. 21 092003 (2008)
- 78. Prozorov R et al., arXiv:0805.2783
- Deutscher G Rev. Mod. Phys. 77 109 (2005) 79
- 80. Chen G-F et al. Chinese Phys. Lett. 25 3403 (2008)
- Sasmal K et al. Phys. Rev. Lett. 101 107007 (2008) 81
- 82. Shein I R, Ivanovskii A L, arXiv:0806.0750
- Krellner C et al. Phys. Rev. B 78 100504(R) (2008) 83.
- Nekrasov I A, Pchelkina Z V, Sadovskii M V Pis'ma Zh. Eksp. Teor. 84 Fiz. 88 155 (2008) [JETP Lett. 88 144 (2008)]
- Ma F, Lu Z-Y, Xiang T, arXiv:0806.3526 85
- Singh D J Phys. Rev. B 78 094511 (2008) 86.
- 87. Liu C et al. Phys. Rev. Lett. 101 177005 (2008)
- Liu H et al. Phys. Rev. B 78 184514 (2008); arXiv:0806.4806 88.
- 89 Zabolotnyy V B et al., arXiv:0808.2454
- Dai J et al., arXiv:0808.0065 90.

- 91. Nakamura H et al., arXiv:0806.4804
- 92. Ding H et al. Europhys. Lett. 83 47001 (2008)
- 93 Zhao L et al. Chinese Phys. Lett. 25 4402 (2008); arXiv:0807.0398
- Li G et al. Phys. Rev. Lett. 101 107004 (2008) 94
- 95 Wray L et al., arXiv:0808.2185
- Mu G et al., arXiv:0808.2941 96
- 97 Altarawneh M M et al. Phys. Rev. B 78 220505 (2008)
- 98. Wang Z-S et al. Phys. Rev. B 78 140501(R) (2008)
- 99. Uemura Y J et al. Phys. Rev. Lett. 66 2665 (1991)
- 100. Ren C et al., arXiv:0808.0805
- Drew A J et al. Phys. Rev. Lett. 101 097010 (2008) 101.
- 102 Aczel A A et al., arXiv:0807.1044
- 103. Goko T et al., arXiv:0808.1425
- 104. Zhang Y et al., arXiv:0808.2738
- 105. Alireza P L et al. J. Phys. Condens. Matter 21 012208 (2009)
- Sefat A S et al. Phys. Rev. Lett. 101 117004 (2008) 106.
- 107 Ning F et al. J. Phys. Soc. Jpn. 77 103705 (2008)
- 108 Qi Y et al. New J. Phys. 10 123003 (2008)
- 109. Leithe-Jasper A et al., arXiv:0807.2223
- Ronning F et al. J. Phys. Condens. Matter 20 342203 (2008) 110.

Huang Q et al. Phys. Rev. Lett. 101 257003 (2008)

Kaneko K et al. Phys. Rev. B 78 212502 (2008)

Yildirim T Phys. Rev. Lett. 101 057010 (2008)

Fang C et al. Phys. Rev. B 77 224509 (2008)

Ren Z et al. Phys. Rev. B 78 052501 (2008)

127. Zhao J et al. Phys. Rev. Lett. 101 167203 (2008)

Subedi A et al. Phys. Rev. B 78 134514 (2008)

Kotegawa H et al. J. Phys. Soc. Jpn. 77 113703 (2008)

Nakai Y et al. J. Phys. Soc. Jpn. 77 073701 (2008)

Fang M H et al. Phys. Rev. B 78 224503 (2008)

Raghu S et al. Phys. Rev. B 77 220503(R) (2008)

142. Hashimoto K et al. Phys. Rev. Lett. 102 017002 (2009)

Grafe H-J et al. Phys. Rev. Lett. 101 047003 (2008)

Nakai Y et al. J. Phys. Soc. Jpn. 77 073701 (2008)

Parker D et al. Phys. Rev. B 78 134524 (2008)

Korshunov M M, Eremin I, arXiv: 0804.1793

Barzykin V, Gorkov L P, arXiv:0806.1933

Chen W et al., arXiv:0808.3234

Boris A V et al., arXiv:0806.1732

Miyake T et al., arXiv:0808.2442

Laad M S et al., arXiv:0810.1607

165. Anisimov V I et al., arXiv:0810.2629

158. Dong J et al. Europhys. Lett. 83 27006 (2008)

Bang Y, Choi H-Y Phys. Rev. B 78 134523 (2008)

Yanagi Y, Yamakawa Y, Ono Y, arXiv:0808.1192

Kurmaev E Z et al. Phys. Rev. B 78 220503(R) (2008)

Chen X H et al. Nature 453 761 (2008)

141. Ding H et al. Europhys. Lett. 83 47001 (2008)

140. Chen T Y et al. Nature 453 1224 (2008)

Malone L et al., arXiv:0806.3908

Hicks C W et al., arXiv:0807.0467

Wu T et al., arXiv:0808.2247

Miclea C F et al., arXiv:0808.2026

Singh Y et al., arXiv:0808.3116

Zhang L et al., arXiv:0808.2653

Hsu F-C et al., arXiv:0807.2369

Liu Z et al., arXiv:0808.1784

Goldman A I et al. Phys. Rev. B 78 100506(R) (2008)

Xu Č, Müller M, Sachdev S Phys. Rev. B 78 020501(R) (2008)

Nekrasov I A, Pchelkina Z V, Sadovskii M V, arXiv:0807.1010

139. Cao C, Hirschfeld P J, Cheng H-P Phys. Rev. B 77 220506(R) (2008)

Chubukov A V, Efremov D V, Eremin I Phys. Rev. B 78 134512

Seo K, Bernevig B A, Hu J Phys. Rev. Lett. 101 206404 (2008);

Parish M M, Hu J, Bernevig B A Phys. Rev. B 78 144514 (2008);

Manousakis E et al. Phys. Rev. B 78 205112 (2008); arXiv:0806.3432

Shorikov A O et al. Zh. Eksp. Teor. Fiz. 135 134 (2009) [JETP 108

Craco L et al. Phys. Rev. B 78 134511 (2008); arXiv:0805.3636

Korshunov M M, Eremin I Phys. Rev. B 78 140509(R) (2008)

Tegel M et al. J. Phys. Condens. Matter 20 452201 (2008) Jeevan H S et al. Phys. Rev. B 78 092406 (2008)

Kumar M et al. Phys. Rev. B 78 184516 (2008) 111.

Su Y et al. Phys. Rev. B 79 064504 (2009)

117. Zhao J et al. Phys. Rev. B 78 140504(R) (2008)

- Torikachvili M S et al. Phys. Rev. Lett. 101 057006 (2008) 112.
- 113. Kreyssig A et al. Phys. Rev. B 78 184517 (2008); arXiv:0807.3032