Structural and electronic properties of LaO$_{0.85}$F$_{0.15}$FeAs superconductor modified under neutron irradiation

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The effect of atomic disorder induced by neutron irradiation on the crystal structure and electronic states near $E_F$ of the lightly overdoped LaO$_{0.85}$F$_{0.15}$FeAs ($T_c = 21 K$) was studied by X-ray diffraction and $^{75}$As NMR. The irradiation of the polycrystalline sample by 'moderate' neutron fluence of $\Phi = (0; 0.5; 1.6) \cdot 10^{19} \text{cm}^{-2}$ at $T = 50^\circ C$ leads to the suppression of superconductivity. It is shown that neutron irradiation produces an anisotropic expansion of the tetragonal lattice almost due to an increase of the Fe-As distance. A partial loss of the 2D character of the FeAs layer is accompanied with a suppression of the gap-like feature in temperature dependence of the spin susceptibility. In the most disordered state the $^{75}$As spin-lattice relaxation rate follows the Korringa law $^{75}T_1^{-1} \sim T$, the thermal behavior being typical for an isotropic motion of the conducting electrons.

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Recent discovery of high-$T_c$ superconductivity in the electron-doped oxypnictides LaO$_{1-x}$F$_x$FeAs gave new impulse in an activity of the superconductivity researches. Similar to superconducting cuprates, the new superconducting materials have layered structure providing an anisotropy of electronic properties, undoped LaOFeAs compound is antiferromagnetic, and superconductivity occurs upon adding either electrons or holes in the FeAs layer. Nevertheless a pseudo gap near the Fermi level was evidenced in the photoemission spectra of FeAs layer. Moreover the pseudogap behavior of spin susceptibility becomes more pronounced with the electron doping approaching to the optimal ($x \approx 0.1$) for superconductivity in LaO$_{1-x}$F$_x$FeAs, whereas it does in the hole-doped Fe-based Ba$_{1-x}$K$_x$Fe$_2$As$_2$ superconductor. It was shown that in the optimally and overdoped compositions of LaO$_{1-x}$F$_x$FeAs ($x > 10$) both the Knight shift and spin-lattice relaxation $T_1^{-1}$ of $^{75}$As and $^{57}$Fe respectively probing the Fermi-liquid ($q \approx 0$) and staggered ($q(\pi, \pi)$) components of spin susceptibility $\chi(q)$ gave no evidence of any q-space structure in spin susceptibility $\chi(q)^2$, that might be expected in the presence of antiferromagnetic spin correlations. of any determined almost by the uniform ($q = 0$) component of spin susceptibility $\chi(q)^2$. It is suggested that pseudogap behavior of spin susceptibility is more relevant to rather complex topology of the Fermi surface including both electron and hole pockets which filling can be varied differently whether electron or holes are doped into the FeAs layer. The $^{75}$As NMR study of the overdoped LaO$_{1-x}$F$_x$FeAs ($x = 0.14$) show clearly an increase of the density of states at the Fermi energy with applying an external pressure additional to the internal "chemical" one.

In this report the structural X-ray and $^{75}$As NMR results are presented for light overdoped polycrystalline LaO$_{0.85}$F$_{0.15}$FeAs ($T_c = 21 K$) affected by neutron irradiation. In fact the neutrons present an unique to create atomic-scale defects uniformly distributed in the lattice and acting like "negative chemical pressure" that expands crystal lattice with negligible variation of the concentration of carriers. It is shown that neutron irradiation produces an anisotropic expansion of the tetragonal lattice mainly due to the displacement of arsenic from equilibrium atomic positions, thus creating structural disorder resulting in a partial loss of the 2D character of the FeAs layer.

Polycrystalline sample of LaO$_{0.85}$F$_{0.15}$FeAs was synthesized as a pellet using two-step solid state reaction and subsequent annealing in vacuum. The pellet was sliced into the plate-like samples which were irradiated with neutron fluence fluence $\Phi = (0; 0.5; 1.6) \cdot 10^{19} \text{cm}^{-2}$ at $T_{IRR} = 50 \pm 10^\circ C$. After irradiation both virgin and irradiated samples were moderately crushed into pow-
The structural characterization of irradiated samples was performed at room temperature by a powder X-ray diffraction technique using Cu – Kα radiation. The diffraction patterns obtained in the range of 2θ = (25 – 5)° confirm a single phase tetragonal structure for each sample studied in this work. The subsequent Rietveld refinement performed within space group P4/nmm results in structural parameters listed in Table 1. An insufficient broadening of the Bragg peaks observed even in the X-ray pattern of the sample with the highest neutron fluence is indicative that structural defects in the sublattices of iron, arsenic are lanthanum are almost relevant to the displacement of atoms from their positions in the ordered material.

| Fluence | 0 | 5×10^{19} cm^{-2} | 1.6×10^{19} cm^{-2} |
|---------|---|--------------------|----------------------|
| Tc, K   | n.s | 4 | 21 |
| a, Å    | 4.0251(5) | 4.0251(6) | 4.0323(6) |
| c, Å    | 8.7017(16) | 8.7207(16) | 8.7710(18) |
| V, Å³   | 140.98(4) | 141.29(4) | 142.61(4) |
| c/a     | 2.162 | 2.167 | 2.175 |
| z_{La}  | 0.1446(7) | 0.1453(21) | 0.1457(12) |
| z_{FeAs}| 0.6501(11) | 0.6522(38) | 0.6639(20) |
| La-O/F, Å | 2.374(3)×4 | 2.381(9)×4 | 2.388(6)×4 |
| Fe-Fe, Å | 2.8462(3)×4 | 2.8462(3)×4 | 2.8513(3)×4 |
| Fe-As, Å | 2.400(3)×4 | 2.410(19)×4 | 2.477(10)×4 |

The main features of the radiation-induced structural disorder are shown in Fig.2. With the neutron fluence increasing a growth of the tetragonal unit cell (Fig.2b) occurs mainly along c direction due to the thicker Fe-As layer in irradiated samples. While the structural parameters of the La-O layer (Table 1) do not show any sufficient variation. It is evident (Fig.2c) that a thickness of the Fe-As layer is growing due to an increase of the Fe-As interatomic distance, whereas the distance d(Fe-Fe) remains practically unchanged. Under neutron irradiation the structural changes of the nearly optimal electron-doped LaO_{0.85}Fe_{0.15}As are developed in the way entirely opposite to those using an effect of "chemical pressure" to optimize Tc in the electron-doped LaO_{1-x}Fe₃As (x > 0.6)\textsuperscript{11} and LaO_{1-x}FeAs\textsuperscript{12} compositions. The cell volume V=144Å of the most disordered nonsuperconducting sample is found above an upper limit of the cell volume values which were reported somewhere for the Fe-based superconducting pnictides\textsuperscript{2}.

The ⁷⁵As NMR measurements were carried out on the home-built pulse-coherent spectrometer in magnetic field of 94 kOe over the temperature range 10-300 K. Each quadrupole broadened ⁷⁵As (\textsuperscript{75}I = 3/2) NMR spectrum was obtained by summing the Fourier-transformed half-echo signals acquired at equidistant operating frequencies. Figure 3 show representative spectral patterns of the central transition (mI = -1/2 - +1/2) measured at room temperature in the LaO_{0.85}Fe_{0.15}As powder samples irradiated by different neutron fluence Φ. The two-
peaked line shape of the transition originates in an interaction of the \(^{75}\text{As}\) nuclear quadrupole moment with the electric field gradient created at arsenic by electronic environment, and the high-frequency peak corresponds to the crystallites with c crystal axis oriented perpendicular \((\theta = 90^\circ)\) to the magnetic field direction. It is remarkable that under neutron irradiation the peak does not show any additional broadening due apparently to induced charge disorder. This NMR observation is completely consistent with X-ray results thus evidencing that local charge symmetry at the As sites does not deviate in average from axial symmetry of the As site in the ordered \((\Phi = 0)\) material.

The \(^{75}\text{As}\) spin-lattice relaxation rate \(T^{-1}_1\) was measured to trace thermal behavior of the spin susceptibility \(\chi_s(q)\) in the normal state of the irradiated \(\text{LaO}_{0.85}\text{Fe}_{0.15}\text{As}\) samples. We measured the \(^{75}\text{As}\) spin-lattice relaxation rate \(T^{-1}_1\) using an inversion recovery method. The nuclear magnetization \(^{75}\text{m}(t)\) was measured by integrating spectral intensity within \(\pm 50\) kHz around a peak \((\theta = 90^\circ)\) of the central transition (Fig. 3). The recovery curve of nuclear magnetization was fitted with an expression \(\{m(\infty) - m(t)\} \sim 0.1 \cdot \exp(-t/T1) + 0.9 \cdot \exp(-6t/T1)\) presuming that hyperfine magnetic interaction of the nuclear spin \(^{75}I = 3/2\) with electronic spin environment is dominating.

The temperature dependence of the \(^{75}\text{As}\) nuclear spin-lattice relaxation rate measured in the neutron irradiated \(\text{LaO}_{0.85}\text{Fe}_{0.15}\text{As}\) samples is presented in Fig. 4 as a product \((T_1T)^{-1}\). In the ordered \((\Phi = 0)\) and lightly irradiated \((\Phi = 0.5 \cdot 10^{19}\text{cm}^{-2})\) superconducting samples \((T_1T)^{-1}\) show gradual decrease from room temperature with nearly constant behavior below 30 K, which is above \(T_c\). Such pseudogap behavior of \((T_1T)^{-1}\) was observed in all electron-doped Fe-based superconductors\(^{2,8}\). Following\(^2\) we have used an expression \(a + b \cdot \exp(-\Delta/T)\) to fit the \((T_1T)^{-1}\) data. The corresponding fitting curves are plotted by solid lines in Fig. 4. As a result, the magnitude of the pseudogap is estimated to be \(\Delta(\Phi = 0) = 168(30)\) K and \(\Delta(\Phi = 0.5 \cdot 10^{19}\text{cm}^{-2}) = 108(20)\) K with \(a = 0.035(6)\) (sK)\(^{-1}\) independent on \(\Phi\) in superconducting samples. The decrease of \(\Delta\) with increase of neutron fluence \(\Phi\) is indicative of that pseudogap behavior of \((T_1T)^{-1}\) originates in the specific 2D band structure near the Fermi energy\(^2\).

In fact, recently reported scaling of \((T_1)^{-1}(T)\) measured in \(\text{LaO}_{0.9}\text{Fe}_{0.1}\text{As}\) at \(57\text{Fe}\), \(^{75}\text{As}\), \(^{139}\text{La}\) and \(^{19}\text{F}\) nuclei of atoms probing spin fluctuations in different areas of the \(q\)-space gives compelling evidence, that dynamic spin susceptibility does not have any strong \(q\)-dependence in the optimally electron-doped oxyxynide.

In the most disordered nonsuperconducting sample of \(\text{LaO}_{0.85}\text{Fe}_{0.15}\text{As}\) the \(^{75}\text{As}\) spin-lattice relaxation rate follows the Korringa law \(T_1^{-1} \sim T\), the thermal behavior being typical for an isotropic spectrum of the quasiparticle excitations near EF. The Curie-like upturn of \(T_1^{-1}\) below \(30\) K is addressed to an additional contribution to \(T_1^{-1}\) due accumulated structural defects, including themselves the localized magnetic moments. The magnetism of localized magnetic moments is seen clearly in the Curie term of the bulk magnetic susceptibility at low temperature. It was found that corresponding Curie constant increases proportionally to the neutron fluence.

In conclusion, an influence of structural disorder induced by neutron irradiation up to the fluence \(\Phi = 1.6 \cdot 10^{19}\text{cm}^{-2}\) on the spin susceptibility was studied in normal state of the lightly overdoped superconducting...
LaO$_{0.85}$F$_{0.15}$FeAs by measuring nuclear spin-lattice relaxation of $^{75}$As. According to the X-ray diffraction data the radiation-induced structural defects remain unchanged the tetragonal symmetry of the irradiated by neutrons LaO$_{0.85}$F$_{0.15}$FeAs. The accumulated disorder results in a growth of the cell volume, almost due to an increase of the Fe-s interatomic distances. A partial loss of the 2D character of the FeAs layer is accompanied with a suppression of the gap-like feature in temperature dependence of the spin susceptibility. In the most disordered state the $^{75}$As spin-lattice relaxation rate follows the Korringa law $^{75}T_1^{-1} \sim T^*$, the thermal behavior being typical for an isotropic motion of the conducting electrons

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