Low-temperature anomalies of EXAFS at the $K$-edge of As in superconducting LaFe$_{0.89}$Co$_{0.11}$AsO

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Abstract. The temperature dependence of the EXAFS-spectra measured above the $K$ absorption edge of As in superconducting ($T_c = 13.5$ K) single crystals of LaFe$_{0.89}$Co$_{0.11}$AsO were investigated. Analysis of the spectra in the harmonic approximation revealed anomalies in the temperature dependence of the Debye-Waller factor for As-Fe interatomic bond which correlated with the temperature dependence of electrical resistivity, the coefficient of thermal expansion and magnetic susceptibility given in literature. Taking into account that similar anomalies were earlier observed in superconducting oxides based on BaBiO$_3$ and in cuprates we conducted the EXAFS spectra analysis in the anharmonic approximation using the potential of arbitrary shape for As-Fe bond vibrations. It was shown that the double-well approximation describes the temperature dependence of the EXAFS spectra better than the harmonic one. The temperature dependence of tunneling frequency and a distance between the wells for double-well potential were obtained. The results indicate that local structural dynamic heterogeneities have a strong impact on macroscopic properties of iron-based superconductors.

1. Introduction
A novel unconventional superconductor LaFe$_{1-x}$Co$_x$AsO, discovered in 2008 [1], belongs to the iron-based family. A comprehensive study of this material is nowadays one of the most attractive, though challenging, problem in physics of high-temperature superconductors (HTSC). Understanding the processes that underlie the formation of the superconducting state in these systems is far from complete and promises to gain insight into the nature of HTSC.

This research concerns the study of the local structure anomalies of superconducting LaFe$_{0.89}$Co$_{0.11}$AsO at low temperature.

2. Results and discussion
High-quality single crystal of superconducting LaFe$_{0.89}$Co$_{0.11}$AsO of rather large size $2\times2\times0.2$ mm$^3$, were grown under ambient pressure in NaAs flux in Ames laboratory, USA [2, 3]. The EXAFS spectra measurements were made in the European Synchrotron Radiation Facility ESRF (Grenoble, France) at BM23 beamline [4]. X-ray absorption spectra were measured in fluorescence mode at the $K$-edge of As in temperature range of 14-300 K with an increment of ~ 10 K. Low-temperature measurements were carried out using a liquid-helium flow cryostat, temperature instabil-
ity didn’t exceed \( \pm 1\) K at 300K and 0.1K at 4K. The double-crystal Si (111) monochromator was detuned to 50% from maximal intensity to eliminate the contributions of higher harmonics.

The polarized As K-edge EXAFS measurements were carried out in the geometry when the crystal was oriented so that the As-Fe bond was parallel to the electric field direction of the photon beam. In this case only one of four tetrahedral As-Fe bonds made a main contribution to the spectra.

The fine oscillatory structure of the absorption spectra was converted to the atomic pair distribution function (PDF) in processing the EXAFS spectra by Fourier transform technique. Consideration of the PDF in [3] as a function of temperature revealed anomalies in the behavior of the first peak of Fourier-transform which corresponded to As-Fe bonds. The amplitude of the peak is determined by the Debye-Waller factor value and therefore should increase monotonically with temperature decreasing due to attenuation of thermal vibrations. However, reported results [3] demonstrated a reverse behavior in the vicinity of 60 and 150 K which was interpreted in the framework of harmonic approach to the EXAFS data analysis as abnormal increase of Debye-Waller factor at given temperature points.

It should be noted that the same temperatures correspond to anomalies in the temperature dependencies of electrical resistivity [5], the coefficient of thermal expansion [6] and magnetic susceptibility [7] of these materials. It clearly demonstrates that the local structure influences on the properties of LaFe\(_{0.89}\)Co\(_{0.11}\)AsO and specially emphasizes the importance of identified anomalies. Therefore, the correct description of these anomalies is a very significant problem.

It's worth mentioning that similar anomalies were observed in cuprates [8-13] and in BaBiO\(_3\)-based [14-16] high-temperature superconductors. It is believed that vibrations in the double-well potential may be responsible for the formation of the superconducting state [12-16]. Our recent studies of iron chalcogenides Fe(TeSe)\(_{1.0}\) [17] have been revealed the correlation of local structure peculiarities and superconducting properties of Fe(TeSe)\(_{1.0}\). Drechsler et al. recently presented a fruitful discussion concerning mechanisms of superconductivity in iron-based superconductors [18]. However, the nature of low-temperature anomalies in these compounds has not been well established so far [20, 21].

In [21] we for the first time successfully applied the concept of a double-well potential to one of the iron-based superconductors – LaFe\(_{1.0}\)Co\(_{0.1}\)AsO.

The reason for the observed anomalies is that the standard harmonic approach for EXAFS spectra processing is incorrect if a bond movement is strongly anharmonic, and one should refer to the more general expression:

\[
\chi(k) = -\sum_n \frac{1}{k} \int |f_n(k, \pi)|^2 \frac{g_n(r)}{r^2} \sin[2kr + 2\delta_n(k) + \phi_n(k, \pi)]dr
\]

with non-Gaussian PDF \( g_n(r) = N_n \sum_{n'} |\Psi_{n'}(r)|^2 \exp(-E_{n'}/kT) \sum \exp(-E_{n'}/kT) \), where \( g_n(r) \) – pair distribution function (PDF); \( N_n \) – coordination number; \( E_{n'} \) and \( \Psi_{n'} \) – \( n' \) energy level and wave function in the model potential.

As a result, the process of fitting the experimental spectra by the new model EXAFS function (1) gives us the shape of the unknown potential \( U \) and atomic pair distribution function \( g \). The treatment was performed by means of FEFF [23] and VIPER [24] software.

Double-well potential consists of two parabolas \( U_1(r) = (a/2)(r - r_1)^2 \) and \( U_2(r) = (b/2)(r - r_2)^2 \). The presence of two equilibrium atomic positions is most likely due to the redistribution of the electron density, which is supposed to occur dynamically, so that there is a shortening or lengthening of the studied bonds. The coefficients of stiffness of parabolas \( a \) and \( b \) are equal and fixed in the current consideration, positions of the wells \( r_1 \) and \( r_2 \) are varied.

Figure 1(a) demonstrates comparative results of both harmonic and anharmonic approach in EXAFS data processing for superconductor LaFe\(_{0.89}\)Co\(_{0.11}\)AsO. The fits of experimental Back Fourier Transforms (BFT) by harmonic and double-well models for the set of key temperatures are shown. It
is seen that double-well model provides a slightly better fit than harmonic one (corresponding experiment-model mismatch factors $R = \left( \frac{\sum |Data_i - Model_i|^2}{\sum |Data_i|^2} \right)^{1/2}$ · 100% are presented in Table 1).

**Table 1.** $R$-factors (quality of the fit) for the treatment of the experimental BFT by conventional harmonic and double-well models for the sets of key temperatures for superconductor LaFe$_{0.89}$Co$_{0.11}$AsO.

| Temperature, K | Harmonic model | Double-well model |
|---------------|----------------|------------------|
| 20            | 19.3           | 16.7             |
| 30            | 19.4           | 20.6             |
| 70            | 20.4           | 16.1             |
| 100           | 24.1           | 17.6             |
| 225           | 21.8           | 21.3             |

**Figure 1.** Comparative fits of experimental Back Fourier Transforms (BFT) by harmonic and double-well models for the set of key temperatures (a), calculated double-well potentials with energy levels (b) and temperature dependence of the distance between the wells (c) for superconductor LaFe$_{0.89}$Co$_{0.11}$AsO.

The calculated double-well potentials for LaFe$_{0.89}$Co$_{0.11}$AsO are shown in Figure 1(b). One can see the change in the shape of potential when passing through the temperatures where anomalies are observed. Namely, when the temperature goes down, there is the decrease in the height of the potential barrier between wells, which accompanied by the increase in the probability of Fe atoms tunneling through the barrier, reflected in [21] by PDF dependencies.

Numerical characteristic of the tunneling process – its frequency – can be determined from the found energy levels $E_1$ and $E_0$ in a double-well potential according to quantum mechanics as $\omega = E_1 - E_0$. Our recent work [21] reported on the temperature dependence of tunneling frequency, from which it is be clear that in the vicinity of the anomalies under discussion the oscillations of Fe atoms in the double-well potential near As are amplified and become more dynamic. This is due to the decrease of the
distance between the wells of the potential (Figure 1(c)), which results in the decrease of the height of the potential barrier, as shown on Figure 1(b).

In addition, it should be noted that tunneling frequencies are in the terahertz range, which is typical for the phonon modes. The study of phonon dispersion may be useful to search for some phonon spectrum features in the temperature range where anomalies are observed. If they are found, this will independently confirm the feasibility of the proposed scenario of dynamical atomic oscillations in the double-well potential.

3. Conclusion
Summarizing all the above, we can conclude that the anomalies in the local crystalline structure of iron-based superconductor LaFe$_{0.89}$Co$_{0.11}$AsO observed by EXAFS may be due to the excitation of Fe atoms vibrations in double-well potential around As atoms, causing, in turn, changes in the temperature dependencies of electrical resistivity, linear thermal expansion and magnetic susceptibility.

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