Crystal and magnetic structure of the oxypnictide superconductor LaO$_{1-x}$F$_x$FeAs: evidence for magnetoelastic coupling

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(Dated: February 23, 2010)

High-resolution and high-flux neutron as well as X-ray powder-diffraction experiments were performed on the oxypnictide series LaO$_{1-x}$F$_x$FeAs with 0 ≤ x ≤ 0.15 in order to study the crystal and magnetic structure. The magnetic symmetry of the undoped compound corresponds to those reported for ReOFeAs (with Re a rare earth) and for AFe$_2$As$_2$ (A=Ba, Sr) materials. We find an ordered magnetic moment of 0.63(1) $\mu_B$ at 2 K in LaOFeAs, which is significantly larger than the values previously reported for this compound. A sizable ordered magnetic moment is observed up to a F-doping of 4.5% whereas there is no magnetic order for a sample with a F concentration of x=0.06. In the undoped sample, several interatomic distances and FeAs tetrahedra angles exhibit pronounced anomalies connected with the broad structural transition and with the onset of magnetism supporting the idea of strong magneto-elastic coupling in this material.

PACS numbers: 61.50.Ks; 74.70.Xa; 75.30.Fv
Keywords:

I. INTRODUCTION

The recently discovered family of oxypnictides superconductors has focused the interest of the scientific community as they represent the first non-copper-oxide based layered superconductors reaching a $T_c$ of 55 K. Their crystal structure is similar to the one adopted by the copper-based superconductors i.e. a layered structure where FeAs sheets are sandwiched by LaO/F sheets (Fig. 1(a)). Like for the cuprates superconductivity arises by chemical doping and suppression of the magnetic ground state; however, also the application of pressure to the non-doped system can induce superconductivity for certain FeAs compounds in clear contrast to the cuprates where the antiferromagnetic state of the parent phase is a Mott-Hubbard insulator requiring electronic doping in order to obtain metallicity and superconductivity. For SmO$_{1-x}$F$_x$FeAs the magnetic ordered state even extends to doping levels within the superconducting regime and low-energy spin fluctuations have been observed up to the doping levels where $T_c$ is maximal. These findings suggest an important role of magnetism in the superconducting pairing.

The magnetism in the FeAs compounds appears to be very sensitive to the structural details which in turn modify the Fermi nesting conditions and the geometric frustration. It has even been stated that the structural distortions play a more important role in the modification of the Fermi surface than charge doping for inducing superconductivity. The shape of the FeAs$_4$ tetrahedra seems to be decisive, as the highest superconducting transition temperatures are obtained for regular FeAs$_4$ tetrahedra. This observation is corroborated by density functional theory calculations which reveal a clear dependence of the Fe magnetic moments as well as of the magnetic interaction parameters on the shape of the FeAs$_4$ layers, i.e. the FeAs bond distance and the layer thickness.

We have combined high-flux and high-resolution neutron and X-ray powder diffraction experiments to study the magnetic and crystal structure of the LaO$_{1-x}$F$_x$FeAs series. We may unambiguously determine the magnetic symmetry of the undoped material finding a sizeable ordered moment. The doping dependence of structural parameters qualitatively confirms earlier studies, but upon
cooling through the structural and magnetic transitions, the pure and slightly doped materials exhibit anomalies in bond distances and in bond angles which reflect the general magnetophonon coupling in FeAs compounds.

II. EXPERIMENTAL

Powder samples of LaO$_{1-x}$F$_x$FeAs have been synthesized using a previously reported two-step solid-state reaction method. We mention that for our sample with the nominal F content $x=0.04$ investigated in this work, wavelength dispersive X-ray analysis yields a higher F content as compared to a sample with the same nominal concentration which has been investigated in previous studies of our group, see for example. We therefore refer to the former sample by using the measured F content ($x=0.045$) in order to discriminate it from the latter and otherwise use the nominal doping levels throughout the paper.

Moreover, we note that for our sample with $x=0$, resistivity measurements suggest $T_S \sim 152$ K (peak of $\rho(T)$) and $T_N \sim 135$ K (inflection point of $\rho(T)$), i.e., at somewhat lower temperatures as have been found in our previous undoped sample.

The nuclear structure investigation of all powder samples ($0 \leq x \leq 0.15$) at room temperature (RT), 200 K, 100 K and 2 K has been carried out at the high-resolution neutron powder diffractometer D2B (Institut Laue-Langevin, Grenoble), where the $x=0$ and 0.045 samples have been examined at additional temperatures. The experiments have been performed using the wavelength of 1.594 Å from the Ge(355) reflection. Powder diffraction patterns have been recorded with a counting time of 3h per temperature point. The magnetic structures of the samples with $0 \leq x \leq 0.06$ have been investigated at the high-flux neutron powder diffractometer D20 (ILL). A wavelength of 2.41 Å emerging from the (002) reflection of a pyrolytic graphite monochromator has been used, which gives a good compromise between high flux and reciprocal space resolution. Diffraction patterns have been recorded for 2h above the magnetic transition and at various temperatures within the magnetically ordered phase. The same samples have been used for further experiments at an X-ray powder diffractometer Siemens D5000. Each X-ray diffraction pattern has been measured for 5h using CuKα radiation.

III. RESULTS AND DISCUSSION

A. Magnetic structure in pure and slightly doped LaOFeAs

The magnetic structure of LaOFeAs has not been unambiguously determined so far. First evidence for a spin-density wave instability was obtained from kinks in the resistivity and in the magnetic susceptibility further supported by electronic-structure calculations. The diffraction experiments by De la Cruz et al. showed that a structural phase transition occurs slightly above the magnetic transition. The structural and magnetic transition temperatures amount to $T_S=155$ K and $T_N=137$ K respectively. However, the nuclear and magnetic structures proposed in Ref. appear very unlikely. As justified in detail below and in agreement with the findings for ReOFeAs and AFe$_2$As$_2$ we will assume an orthorhombic and not a monoclinic low-temperature phase in the following. The orthorhombic $a_o$ and $b_o$ axes are rotated by 45° degrees with respect to the tetragonal axes $a_{tet}$. The proposed magnetic structure consists of ferromagnetic stripes of neighboring Fe moments running along an orthorhombic axis antiferromagnetically stacked along the perpendicular axis, see Fig. (c). In the model proposed in Ref. the stacking vector $q_{stack}$ is perpendicular to the magnetic moment $m_{Fe}$ which amounts to 0.36(5) $\mu_B$ at $T\sim 8$ K. A following neutron diffraction experiment on LaOFeAs by McGuire et al. also reports a moment of 0.35 $\mu_B$ but does not discuss the spin orientation. Huang et al. describe a magnetic structure with $q_{stack}$ parallel to the magnetic moment $m_{Fe}$, which disagrees with the earlier report but apparently the instrument resolution is insufficient to determine the spin direction along $a_o$ or $b_o$.

We have analyzed all powder diffraction patterns using the FullProf program. The structural investigation at the high-resolution diffractometer D2B confirmed the correct phase formation of the tetragonal $P4/nmm$ and orthorhombic $Cmme$ structures above and below the structural phase transition, respectively, see below. In order to focus on the weak magnetic scattering the D20 diffraction patterns of the paramagnetic phases have been subtracted from the respective patterns of the magnetically ordered phases. For the undoped sample the differences are manifest in two well defined magnetic peaks, indexed as (10$\bar{0}$) and (10$\bar{2}$) at $2\theta = 25.8^\circ$ and 34.6$^\circ$, respectively, to which a magnetic structure model has been refined (Fig. 2). Representation analysis has been used to derive those magnetic structure models which are compatible with the nuclear structure ($Cmme$) and with the propagation vector with a half-indexed $c^*$-component and an antiferromagnetic coupling between two Fe moments related by the C centering: $(1\;0\;\frac{1}{2})$. Out of the six possible collinear spin configurations (three directions along the principal crystallographic axes and the coupling between the two moments chosen at (0.25,0.0,0.5) and (0.75,0.0,0.5) in orthorhombic notation) only two may describe the data sufficiently well. These are the models with $q_{stack}$ parallel to the magnetic moment $m_{Fe}$. Since neutron diffraction only measures the magnetic component perpendicular to the scattering vector, the models with $q_{stack}$ perpendicular to the magnetic moment $m_{Fe}$ proposed in Ref. can be clearly excluded. To decide between the alignment of the magnetic moments along $a_o$ or $b_o$ is more difficult, but due to the high statistics and
resolution of the D20 data this is possible as well. The solid (black) and dashed lines in Fig. [2] show the calculated patterns corresponding to the models where the moments are aligned along the $a_o$ axis and along the $b_o$ axis, respectively. As the $b_o$ axis is $0.4\%$ shorter compared to $a_o$ the two models can be distinguished. The model with the magnetic moments along the $a$ axis is better suited to describe the observed peaks which is also expressed by the respective R values ($10.71\%$ for $\mu||a$ and $12.76\%$ for $\mu||b$). The Fe magnetic moment along the $a$ axis has been refined to $0.63(1) \mu_B$ which is about twice the size of the magnetic moment presented in Refs. [19] and [20]. The ordered moment at the Fe site still seems to be substantially lower than in other undoped FeAs compounds [25] but the difference is much smaller than previously reported.

The same magnetic model was used to describe the data for the slightly doped samples. The refined magnetic moments for the $x=0.02$ and $x=0.045$ samples are $0.59(2) \mu_B$ and $0.32(2) \mu_B$, respectively. For samples with $x \geq 0.06$ no magnetic scattering could be observed. The three powder samples revealing magnetic order have been investigated in more detail as a function of temperature. Fig. [3] shows the temperature and doping dependent suppression of the magnetic order. One can observe that the undoped and the $x=0.02$ sample exhibits similar magnetic moments with a similar temperature dependence, but the magnetic reflections of the doped sample exhibit a slightly broader full width at half maximum (FWHM) than those of the undoped sample (Fig. [4]). A decrease of the coherence length would be in perfect agreement with the subsequent suppression of magnetic order, which is then expressed by the strongly reduced magnetic moment for $x=0.045$ and finally by the absence of long-range order for $x=0.06$. However, we may not fully rule out that the broadening of the magnetic peaks is due to an incommensurate magnetic order; but in case of the $x=0.02$ sample such an effect must be small.

**B. Crystal structure in LaOFeAs**

The crystal structure of LaOFeAs was studied by high-resolution neutron diffraction and by x-ray powder diffraction. The structural phase transition forms the most prominent feature in the temperature dependence of the crystal structure. In agreement with most pre-
vious studies we find that the low-temperature phase is orthorhombic, space group Cmme; the refinement of the structure model in the monoclinic space group proposed in Ref. 19 did not yield a better data description; the structural parameters given in Ref. 19 clearly worsen the reliability factors. However, the phase transition from $P4/nmm$ to Cmme seems to be quite uncommon. This transition is of the proper ferroelastic character and it can be directly related to the magnetism. The magnetic order at low temperature exhibits an orthorhombic symmetry due to the alignment and the stacking of the ferromagnetic stripes and due to the fixed orientation of the magnetic moments. Therefore, the crystal structure in the magnetic phase must become orthorhombic.

There is, however, another role of the orthorhombic distortion: It lifts the magnetic frustration. The magnetic structure is stabilized by a large next-nearest neighbor Fe-Fe interaction (along the diagonals of the Fe square lattice, see Fig. 1(b)), but within the tetragonal symmetry the nearest-neighbor interactions are fully frustrated yielding two antiferromagnetic sublattices which are completely decoupled. Depending on the arbitrary choice of the coupling of the two subsystems, the ferromagnetic stripes run either along the $a$ or along the $b$ directions in orthorhombic notation. It is thus the role of the tetragonal-to-orthorhombic phase transition to lift the magnetic degeneracy and the frustration very similar to the magneto-elastic coupling recently studied in VOCl.

The occurrence of magnetism in LaOFeAs can be considered as an electronic nematic phase, but the magnetic in-plane anisotropy is only a natural consequence of the fact that the magnetic structure breaks the tetragonal rotation axis. The similarity with liquid-crystal phases is furthermore limited, as the high-temperature phase in LaOFeAs only exhibits a four-fold and not a continuous rotations symmetry. Nevertheless, one may associate the orthorhombic phase and its precursors with an electronic nematic state, and indeed resistivity measurements on detwinned Ba(Fe/Co)$_2$As$_2$ crystals reveal a pronounced electronic anisotropy.

At low temperature the orthorhombic splitting in LaOFeAs is well documented for example by the neutron diffraction profiles of the (400)/(040) reflections, see Figure 5. Close to the structural transition these two reflections, however, overlap due to the smaller orthorhombicity in the neutron and in the X-ray experiments. The neutron data were used to refine the orthorhombic structure model up to 180 K and with the X-ray data we fitted the total width of the (400)/(040) scattering. Considering the steepest temperature dependencies of the orthorhombicity and of the peak width, one may determine the structural transition temperature to about $T_s \sim 150$ K, which perfectly coincides with the well-defined kink in the resistivity and with the maximum in the thermal expansion coefficient both measured on nearly identical samples. However, the broadening of the (400)/(040) scattering as well as a finite orthorhombicity remain clearly visible above $T_s$, they only vanish at a temperature of about 200 K. These findings fully agree with similar diffraction studies by McGuire et al. and by Nomura et al. indicating that this feature is not sample specific but an intrinsic property of LaOFeAs. Great care is thus needed to determine the true structural phase transition temperature in LaO$_{1-x}$F$_x$FeAs with the aid of diffraction data only. The broadening of the peaks in the intermediate temperature range should be interpreted as an inhomogeneous phase with strong local orthorhombic distortions as precursors of the long-range transition. The correlation length of the local orthorhombic distortions must be rather large, of the order of the coherence length of the radiation, i.e. of the order of several hundreds of Angstroems. The broad temperature range, where orthorhombic precursors exist, seems to coincide with the upturn of the thermal expansion coefficient well above the long-range structural transition and with the upturn in the electric resistivity. Evidence for orthorhombic precursors can also be deduced from the resistivity measurements on detwinned Ba(Fe/Co)$_2$As$_2$ crystals, as the anisotropy sets in already above the long-range structural transition.

The high-resolution neutron data were used to refine structure models varying the cell constants, the z component of the La and As positions and the isotropic temperature factors of all species. From the refined parameters (see Tab. I) further structural aspects like interatomic distances and angles have been deduced, see Fig. 5.

The temperature dependence of several structural aspects is shown in Figs. 7(c) and (d) for $x=0$ and $x=0.15$, respectively. The lattice constants show an expected dependence on temperature, but the remaining parameters reveal interesting features around the structural phase transition. In LaOFeAs, the interatomic distances and
Therefore, all diffraction anomalies in LaOFeAs.

The orthorhombic precursors and the structural anomalies appear to be closely related with the electronic and magnetic properties. In the temperature range of the orthorhombic precursors the resistivity shows an upturn, whereas the long-range orthorhombic transition finally induces a decrease in resistivity, see for example Ref.\textsuperscript{13}. The magnetic importance of the structural transition is visible in the reduction of the magnetic susceptibility which can be interpreted by either a suppression of ferromagnetic fluctuations or an increase of the antiferromagnetic interaction. It appears interesting to note that the structural anomalies observed concern those structural parameters which are determining the size of the Fe moment, i.e. the FeAs distance and the FeAs layer thickness.\textsuperscript{12} Furthermore, the structural anomalies indicate extrema in the temperature dependencies of the respective parameters, whereas a simple structural transition should induce a kink or a jump in the temperature patterns have been analyzed as well with the microstrain option implemented in FullProf, which introduces an orthorhombic distortion into a tetragonal cell. The parameters obtained by this refinement method proved to be equivalent within the error bars. Additionally, a diffraction pattern from within the transition regime has been analyzed using two refined structural models of a tetragonal (just before the transition) and an orthorhombic phase (just after the transition) by simply refining the respective scale factors. This procedure led to a considerably worse agreement implying that the broadening of the structural transition is a system-inherent property and not due to inhomogeneities in the chemical composition.

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dependency. These extrema, however, agree nicely with the anomalous contribution to the thermal expansion, which exhibits a sign change in the same temperature range and thus also yields an extremum for the anomalous component of the lattice volume.\textsuperscript{16}

C. Doping dependence of the crystal structure in LaO$_{1-x}$F$_x$FeAs

The tetragonal to orthorhombic transition has been studied by neutron diffraction in detail for two samples with $x=0$ and 0.045 and is represented in Fig. 6\textsuperscript{15} by the orthorhombicity $(a-b)/(a+b)$. From the additional X-ray diffraction experiments, also including the $x=0.02$ and 0.06 samples, the temperature dependent evolution of the FWHM of the splitting $(220)_T$ reflection has been extracted, where the obtained values have been normalized to the FWHM at RT.

It can be seen for $x \leq 0.045$ that the splitting of the $a$ and $b$ lattice constants in an orthorhombic fit, and therefore the broadening of the affected Bragg peaks, sets in well above the transition temperatures given in the literature.\textsuperscript{13,20,30} No high-resolution neutron data has been collected for the $x=0.02$ sample between 100 K and 200 K, but the increase of the FWHM obtained by the X-ray experiments yields a broad transition regime very similar to the observation in the pure compound. The smearing of the structural phase transition by orthorhombic precursors is thus present over a finite doping interval. At the intermediate doping $x=0.045$, it is difficult to determine the structural transition temperature with the diffraction data, as the transition between the precursors and the long-range orthorhombic phase seems to be quite sluggish. The $x=0.06$ sample does not exhibit a comparable peak broadening indicating that the orthorhombic distortion is suppressed in the superconducting phase in LaO$_{1-x}$F$_x$FeAs. Note that also the previously studied superconducting sample with $x=0.05$ did not show the large peak broadening\textsuperscript{32} in contrast with the non-superconducting $x=0.045$ sample studied here. In spite of the strong precursors associated with the structural transition, the long-range orthorhombic distortion seems to become very rapidly suppressed near $x=0.05$ i.e. at the boundary between superconducting and non-superconducting samples. However we may not fully rule out that some orthorhombic precursors persist into the superconducting phase.

The structural phase transition as a function of $F$ doping is located at 0.045 < $x$ < 0.06, evidenced by the merging of the different Fe-Fe/La-As distances and As-Fe-As angles, which is shown in Fig. 7(a) for $T=2$ K. The doping dependent evolution of the structural parameters does not exhibit any significant differences between $T=2$ K and RT (Fig. 7(b)), although the structural phase transition is only observed below 150 K. The lattice parameter $c$ as well as the La-As distance decrease monotonically as a consequence of the charge carrier injection causing a Coulomb attraction of the LaO/F and FeAs layers. On the other hand the charge carrier injection into the FeAs layer leads to an increase of the Fe-As distance and of the As-Fe-As block thickness. The doping causes the FeAs$_4$ tetrahedra to become more homogeneous which is expressed by the different As-Fe-As angles approaching the perfect angle of 109.47°. Our findings are similar to those presented in Ref. 51 but extending to higher F concentrations.

The temperature dependence of the same structural aspects is shown in Figs. 7(d) for $x=0.15$. For this superconducting sample we find no structural anomaly in the temperature dependencies.

IV. CONCLUSIONS

We have performed high-resolution and high-flux neutron powder diffraction experiments on the oxypnictide series LaO$_{1-x}$F$_x$FeAs, which on the one hand confirm the structural parameters and their evolution with $F$-doping reported previously, but on the other hand our results indicate a structural anomaly and a larger magnetic order parameter.

With the high-resolution and good statistics of the diffraction data taken on the D20 diffractometer, we may unambiguously determine the magnetic structure in LaOFeAs obtaining a Fe magnetic moment of 0.63(1) $\mu_B$ which is in good agreement with a previous NMR study,\textsuperscript{22} but about a factor two higher than previous neutron diffraction, muon spin relaxation and Mößbauer reports. The Fe magnetic moment has been subject of debate as it is largely reduced compared to the theoretically expected value of almost 2 $\mu_B$.\textsuperscript{23} Furthermore, the moment alignment is along the $a$ axis parallel to the stacking direction of the ferromagnetic Fe stripes, which fully agrees with the magnetic structure observed in other FeAs compounds. The 2% doped sample exhibits a similarly large magnetic moment, but from the magnetic reflection profile, i.e. from a broader FWHM, a perturbation of the static magnetic order can be deduced. We still find a sizeable ordered moment for a non-superconducting sample with $x=0.045$ in good agreement with muon spin relaxation and Mößbauerer results.\textsuperscript{25} Since this doping level is very close to the superconducting part of the phase diagram, one may deduce a well-defined phase boundary in between.

Concerning the structural properties, we have observed that the tetragonal-to-orthorhombic phase transition extends to a rather large temperature regime with pronounced precursors persisting well above the long-range transition temperature. It is difficult to determine the transition temperature by diffraction techniques as long-range and short-range distortions are nearly impossible to separate. The analysis of the peak height of the nuclear Bragg peaks is certainly misleading. Similar precursor effects should also exist for the ReO$_{1-x}$F$_x$FeAs materials and might be one reason for discrepancies in
FIG. 7: (Color online) Structural parameters of the LaO$_{1-x}$F$_x$FeAs compounds as a function of F doping [(a) T = 2 K, (b) T = RT] and temperature [(c) $x = 0$, (d) $x = 0.15$]. (Black) squares and (red) dots correspond to the left abscissa, while (green) triangles belong to the right one. The grey shaded area in (a) denotes the doping dependent structural phase transition regime. In (c) the dashed line marks the onset of static magnetism while the dotted line indicates the structural phase transition as taken from Ref. 13. Solid lines are guides to the eye.

the phase diagrams obtained by different groups. In LaO$_{1-x}$F$_x$FeAs the long-range orthorhombic distortion is fully suppressed by amounts of doping which are below the level needed to induce superconductivity. Taking further account of the magnetic neutron diffraction results, we confirm the phase diagram presented in Ref. 13. However, we may not exclude that some orthorhombic precursors persist into the superconducting phase in LaO$_{1-x}$F$_x$FeAs as well as in other ReO$_{1-x}$F$_x$FeAs series.

In pure and low-doped LaO$_{1-x}$F$_x$FeAs, the onset of static magnetism as obtained by muon spin relaxation and by the temperature dependence of the magnetic Bragg peaks lies within the broad regime of the tetragonal-to-orthorhombic transition. For pure LaOFeAs, we find structural anomalies just above the onset of magnetism, as the FeAs distance and the FeAs layer thickness pass through a minimum in agreement with the effect observed for the thermal-expansion coefficient. These features seem to arise from the strong magnetoelastic coupling between the shape of the FeAs tetrahedra and the size of the magnetic moment suggesting that the enhancement of the antiferromagnetic correlations through the orthorhombic distortion implies a variation of the magnetic moment.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 608.
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