

Retention of the Tetragonal to Orthorhombic Structural Transition in F-Substituted SmFeAsO: A New Phase Diagram for SmFeAs(O_{1-x}F_x)

A. Martinelli,¹ A. Palenzona,¹ M. Tropeano,¹ M. Putti,^{1,2} C. Ferdeghini,¹ G. Profeta,³ and E. Emerich⁴

¹SPIN-CNR, corso Perrone 24, 16152 Genova, Italy

²Dipartimento di Fisica, Università di Genova, via Dodecaneso 33, 16146 Genova, Italy

³CNR and Dipartimento di Fisica, Università de L'Aquila, Via Vetoio, 10 I-67010 Coppito, Italy

⁴SNBL at ESRF, 6 rue Jules Horowitz, 38043 Grenoble, France

(Received 8 February 2011; published 1 June 2011)

In this Letter we propose a new phase diagram for the SmFeAs(O_{1-x}F_x) system, based on careful analysis of synchrotron powder diffraction data, SQUID, and muon spin rotation measurements. The tetragonal to orthorhombic structural transition is slightly affected by F content and is retained for the superconducting samples, even at optimal doping. These findings relate the AFM transition on a different ground with respect to the structural one and suggests that orbital ordering could be the driving force for symmetry breaking.

DOI: 10.1103/PhysRevLett.106.227001

PACS numbers: 74.70.Xa, 61.05.cp, 81.30.-t

After the discovery of a relatively high superconducting transition temperature (T_c) in LaFeAs(O_{1-x}F_x) by Kamihara *et al.* [1], many investigations were carried out on compounds belonging to the class of compounds referred to as oxy-pnictide and characterized by the general formula REFeAs(O_{1-x}F_x) (RE: rare earth). At room temperature these compounds crystallize in the tetragonal system ($P4/nmm$ space group), whereas on cooling, according to what is reported in literature, they undergo a tetragonal to orthorhombic structural transition at T_{T-O} if F content does not exceed a critical value [2–6]. This structural transition is located between 155–180 K in LaFeAsO [3,7,8], below 150 K for NdFeAsO [2,9], at ~ 158 K in CeFeAsO [6], between 130 and 160 K in SmFeAsO [4,10,11]; according to the literature the progressive F substitution (acting as electron donor) decreases T_{T-O} down to the suppression of the transition and the tetragonal structure is retained on cooling. In pure and slightly F-substituted compounds a long-range spin density wave (SDW) type antiferromagnetic order takes place at T_{SDW} , below T_{T-O} ; as the F content increases the T_{SDW} decreases up to a critical value of F substitution over which the SDW is suppressed in favor of superconductivity (SC). Noteworthy superconductivity can arise within the orthorhombic phase within a selected range of F content [4].

Superconductivity can be induced in this class of compounds also by means of hole doping; it is worth noting that in hole-doped samples T_c is slightly dependent on the elemental rare-earth and reaches values around 15 K at the optimal doping [12,13]. Conversely to what is reported for the electron-doped compounds, in the hole-doped compound (Nd_{1-x}Sr_x)FeAsO, the tetragonal to orthorhombic structural transition is unaffected by the amount of chemical substitution [14] and at low temperature the orthorhombic structure is stable also for samples with $T_c = 13.5$ K, that is characterized by nearly optimal doping.

In this Letter we describe the dependence of the structural transition in SmFeAs(O_{1-x}F_x) on F content that has been studied by analyzing the evolution of the 110 peak behavior between room temperature and 90 K. Details concerning the sample preparation are reported elsewhere [15]. These same samples have been deeply investigated through magnetization, magnetoconductance, μ -SR measurements, revealing optimal properties and compositional homogeneity. High resolution synchrotron powder diffraction analysis was carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) at the BM1B beam line. Data were collected between 90 and 290 K ($\lambda = 0.50663$ Å; step = 0.004° 2θ ; angular range = 1.0 – 55° 2θ) and structural refinement was carried out applying the Rietveld method using the program FULLPROF [16]. The peak shape was modeled using a Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry function coupled with an instrumental file in order to evaluate structural microstrain. In order to carefully evaluate the temperature at which the structural transition takes place, high statistic thermodiffractograms of the 110 diffraction peak (tetragonal indexing) were acquired on cooling (30 K/h) in a continuous scanning mode for samples with $x = 0.00, 0.05, 0.075, 0.10, 0.20$; in fact the 110 tetragonal peak splits into the $020 + 200$ orthorhombic lines on cooling, signaling the symmetry breaking. The experimental setup prevents recording the temperature at which each analytical file is acquired and hence the temperature was estimated on a chronological basis, thus suffering of a few uncertainties that can be estimated as ± 10 K at maximum.

The investigated samples belong to a very well characterized series; in particular, by means of muon spin rotation (μ -SR) the occurrence of a SDW at the FeAs layer has been ascertained in the specimens with x up to 0.085, whereas in SmFeAs(O_{0.90}F_{0.10}) magnetic ordering is

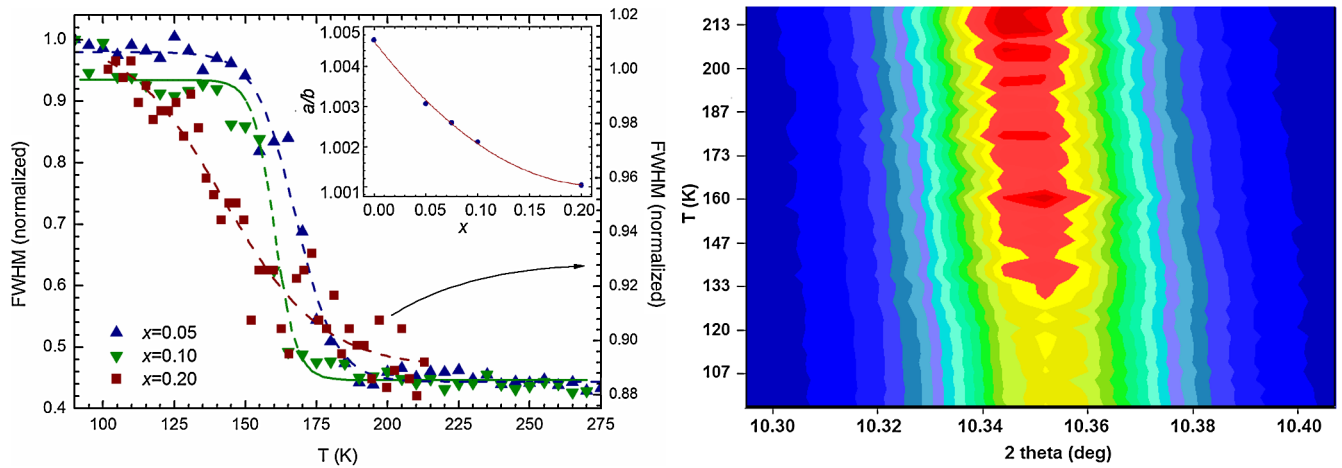


FIG. 1 (color online). On the left: evolution of the FWHM (normalized) for the 110 peak in three samples with different F content (dashed lines are sigmoidal fits of the data); the inset shows the decrease of the orthorhombic distortion as a function of F content (data collected at 90 K). On the right: evolution of the 110 peak on cooling for the sample $\text{SmFeAs}(\text{O}_{0.80}\text{F}_{0.20})$: a dramatic suppression of the intensity is observed below ~ 130 K, coupled with the abrupt FWHM broadening plotted in the panel on the left.

completely suppressed [17]. Moreover, these measurements revealed the nanoscopic coexistence of magnetic order and superconductivity in a very narrow compositional range located around $x = 0.085$.

Figure 1, on the left, shows the evolution of the full width at half maximum (FWHM; normalized data) for the 110 peak (tetragonal indexing) in three samples with different F content obtained by fitting the high statistic data. An abrupt increase of the FWHM is evident on cooling for all the three samples; this increase can be related to the structural transition. In fact none of these samples shows a resolved peak splitting (at least up to 90 K), but we observed a similar behavior for SmFeAsO between 160 and 170 K (not reported in the figure for clarity), in good agreement with the T_{T-O} reported by Hess *et al.* [11] (~ 160 K), within the experimental error, and consistent with the findings of Kamihara *et al.* [10] (~ 150 K). Noteworthy McGuire *et al.* [8] carried out a similar analysis of the FWHM for LaFeAsO ; as a result a significant broadening of the 110 peak was observed below 180 K, where the orthorhombic structural model gives a better fit. More recently the same kind of analysis has been also applied to determine the structural transition temperature in $(\text{La}_{1-y}\text{Y}_y)\text{FeAsO}$ and $\text{Ba}(\text{Fe}_{1-x}\text{Cr}_x)_2\text{As}_2$ compounds [18,19].

Figure 1, on the right, shows the evolution of the 110 peak intensity on cooling for the optimally doped sample $\text{SmFeAs}(\text{O}_{0.80}\text{F}_{0.20})$: a dramatic suppression of the peak intensity is observed below ~ 130 K, a feature coupled with the abrupt increase of its FWHM plotted in the panel on the left. These results suggest that F substitution does not prevent the tetragonal to orthorhombic phase transition, whereas only a slight decrease of T_{T-O} takes place with the increase of F content.

Now we will analyze in detail the structural features of the sample $\text{SmFeAs}(\text{O}_{0.90}\text{F}_{0.10})$. This specimen is

characterized by a relatively high T_c (~ 41 K) and by a completely suppressed magnetic ordering, as revealed by μ -SR measurements [17]. Hence it is representative for the superconductive region of the electronic phase diagram for the system $\text{SmFeAs}(\text{O}_{1-x}\text{F}_x)$. Figure 2, on the left, shows the comparison of the 110 peak for the sample $\text{SmFeAs}(\text{O}_{0.90}\text{F}_{0.10})$ collected at 290 and 90 K (high statistic data): an anisotropic broadening of the peak towards high angle, originated by symmetry breaking is evident.

As a result at 290 K a Gaussian curve satisfactorily fits the peak, whereas at 90 K the fit is notably worsened (Fig. 2, panels on the right), thus indicating that the peak at this temperature cannot be modeled using a unique Gaussian curve.

Taking into account the results obtained analyzing the FWHM, Rietveld refinement for $\text{SmFeAs}(\text{O}_{0.90}\text{F}_{0.10})$ was carried out assuming a tetragonal structural model ($P4/nmm$ structural model) for $T > 170$ K and an orthorhombic one ($Cmme$ structural model) for $T < 170$ K;

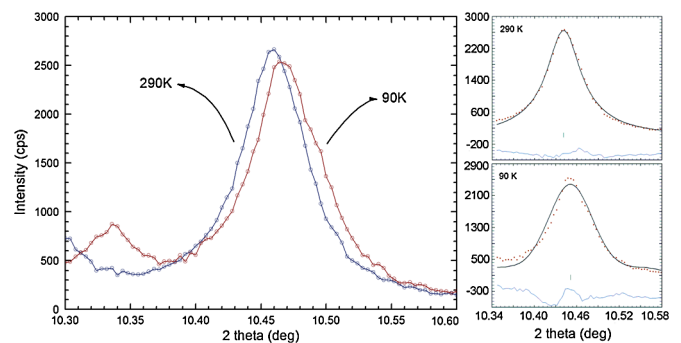


FIG. 2 (color online). On the left: high intensity—high resolution data collected at 290 and 90 K in the 110 peak region for the sample $\text{SmFeAs}(\text{O}_{0.90}\text{F}_{0.10})$. On the right: the two peaks fitted with a single Gaussian-type curve.

Fig. 3 shows the Rietveld refinement plot obtained using the data collected at 90 K. The inset of Fig. 3 is an enlarged view, in the region of the 110 tetragonal peak, of the Rietveld refinement plots carried out assuming a tetragonal (on the left) and an orthorhombic (on the right) structural model (these data must not be confused with the high statistic ones collected only on the 110 peak reported in Fig. 3): it is evident that the orthorhombic structural model provides a better fit than the tetragonal one. This result is confirmed by comparing the R factors obtained applying the tetragonal ($R - \text{Bragg} = 3.39\%$; $R - \text{structure factor} = 2.65\%$) and orthorhombic ($R - \text{Bragg} = 3.26\%$; $R - \text{structure factor} = 2.53\%$) structural models. No discontinuity in specific volume around T_{T-O} is detected, similarly to what was observed for $(\text{La}_{1-y}\text{Y}_y)\text{FeAsO}$ compounds [18].

It is worth noting that in none of the F-substituted sample a resolved peak splitting is observed; at least for lightly doped samples, this is related to the fact that the lowest temperature available during our measurements was 90 K. Moreover, we observed a decrease of the orthorhombic distortion in $\text{SmFeAs}(\text{O}_{1-x}\text{F}_x)$ with the increase of F content (inset of Fig. 1, on the left); from the experimental point of view this phenomenon determines a decrease of the angular distance between the 020 and 200 lines that progressively merge and convolute into a unique peak, masking the symmetry breaking. This phenomenon explains why in literature the structural transition of electron-doped samples is generally reported to be strongly affected by F content, with a dramatic decrease of T_{T-O} even for a relatively low amount of substitution. In fact the occurrence of the orthorhombic phase is generally related to the appearance of $hh0$ peak splitting; in the case

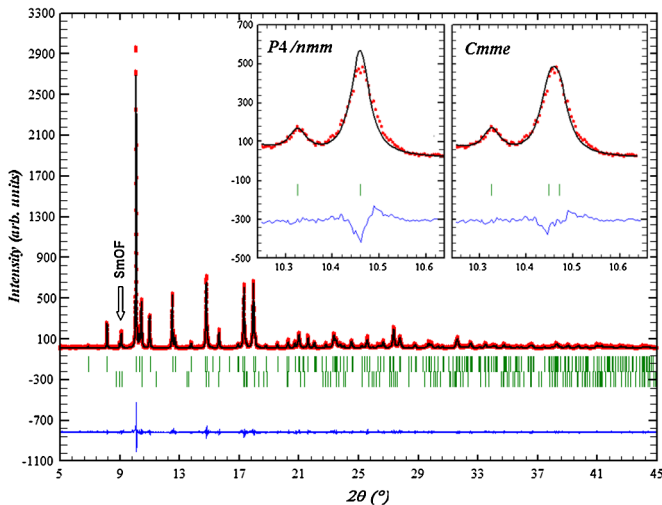


FIG. 3 (color online). Rietveld refinement plot of the sample $\text{SmFeAs}(\text{O}_{0.90}\text{F}_{0.10})$ (data collected at 90 K); the inset is an enlarged view, in the region of the 110 tetragonal peak, of the Rietveld refinement plots carried out assuming a tetragonal (on the left) and an orthorhombic (on the right) structural model.

of low instrumental resolution and/or low amplitude of the orthorhombic distortion, peak splitting can be masked and hence the onset or the occurrence of the structural transition is hidden. In this case only an accurate analysis of the evolution of 110 peak on cooling can reveal structural changes.

Information on compositional homogeneity, in our case the distribution of F within the sample, was provided by line broadening analysis (details will be reported elsewhere). Within the tetragonal system, peak broadening depends on the square cosine of the angle φ between the diffraction vector and the c direction [20] and an increase of the peak breadth should be observed with the decrease of the angle φ . Such a kind of broadening is negligible in our samples, indicating that F is homogeneously distributed within the sample. Hence the observed orthorhombic distortion is not a local feature related to an inhomogeneous distribution of F, but occurs within the whole sample.

These observations concerning the dependence of the structural transition with F substitution reconcile the apparently contradictory findings reported in literature for the tetragonal to orthorhombic transition in electron- and hole-doped compounds. In fact in the electron-doped compounds a strong decrease of T_{T-O} is reported with the increase of F content, and the transition is completely suppressed at optimal doping. Conversely the transition is unaffected by the amount of alkaline-earth in the case of hole-doping and the pure and optimally doped compounds exhibits nearly the same T_{T-O} [14].

Integrating the results of the present work with those obtained by μ -SR and SQUID measurements [17] on the same samples a new phase diagram for the system $\text{SmFeAs}(\text{O}_{1-x}\text{F}_x)$ (x up to 0.20) has been drawn, reported in Fig. 4. This phase diagram is considerably different from those reported in literature [4,10,11]. Here the O-T phase boundary exhibits a slight decrease with increasing F content; conversely the orthorhombic phase boundary is discontinuous in several phase diagrams of 1111-type compounds (see [10,21,22] for reference), apparently

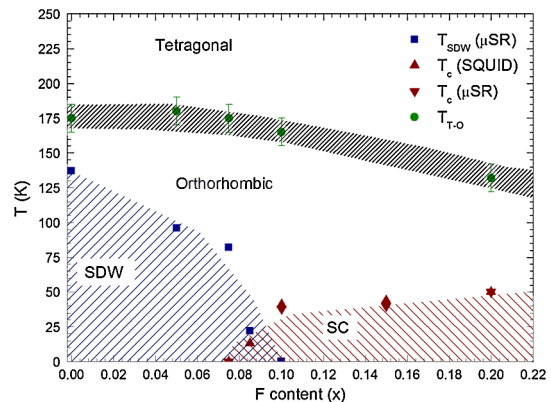


FIG. 4 (color online). The phase diagram of the $\text{SmFeAs}(\text{O}_{1-x}\text{F}_x)$ system up to $x \leq 0.20$.

contrasting some thermodynamic principles. In fact a phase diagram is a graphical representation of thermodynamic variables values at equilibrium and must obey thermodynamic rules. One of these rules states that the extension of a boundary of a 2-phase region must pass into the adjacent 2-phase region and not into a 1-phase one; hence the often reported vertical line separating the orthorhombic region from the tetragonal one at a specific F concentration is meaningless from the thermodynamic point of view. Moreover, the phase boundary cannot be discontinuous because the partial enthalpy and derivative of the partial Gibbs energy changes continuously at phase boundary and the slope must be continuous as well. Such inconsistent phase boundaries are originated by the difficulty to determine the occurrence of the structural transition with the increase of F content because of the decrease of the orthorhombic distortion.

The phase diagram drawn in Fig. 4 can help to improve the understanding of the complicated interplay between structural, orbital, magnetic, and carrier degree of freedom. The nature of the structural transition has been lengthily debated; it has been proposed that symmetry breaking is magnetically driven, relieving magnetic frustration resulting from AFM near-neighbor and next-neighbor interactions between local Fe moments [23–25]. Otherwise also a nematic nature of the structural transition has been suggested, as a consequence of magnetic interactions [26]. Conversely the absence of discontinuity in specific volume [18] around T_{T-O} provides evidence that orbital ordering drives the structural transition, as also theoretically suggested [27–29].

The results presented in this work can be interpreted as a signature of the effects of orbital ordered phases in which the structural distortion and the magnetic transition decouples as a function of doping. The increase of the FWHM on cooling signs the onset of a structural phase transition, evidently not driven by magnetic fluctuations. The occurrence of a symmetry breaking for $x \geq 0.10$, coupled with the complete suppression of magnetic ordering as revealed by μ -SR, suggests that orbital ordering could be the driving force for the transition. We provide evidence that this mechanism is only slightly doping dependent, up to 20%. This reconciles the apparently contradictory findings reported in literature for the tetragonal to orthorhombic transition in electron- and hole-doped compounds, almost unaffected by alkaline-earth content in the latter case.

The scenario proposed in this work relates the AFM transition on a different ground with respect to the structural one. It would be interesting to investigate the orbital ordered phase as a function of doping: if charge doping is detrimental for the nesting properties guiding the SDW transition, it can promote further asymmetries in the dxz/dyz density of states, enhancing the orbital ordered phase.

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