# Effect of chemical pressure on spin density wave and superconductivity in undoped and 15% F-doped La$_{1-y}$Y$_y$FeAsO compounds

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We present a study concerning the partial substitution of yttrium at the lanthanum site of the undoped LaFeAsO and superconducting LaFeAsO$_{0.85}$F$_{0.15}$ compounds. We prepared samples with a nominal yttrium content up to 70% producing simultaneous shrinkage of both the $a$- and $c$-lattice parameters by 1.8% and 1.7%, respectively. The chemical pressure provided by the partial substitution with this smaller ion size causes a lowering of the spin density wave temperature in the undoped compounds, as well as an increase in the superconducting transition temperatures in the doped ones. The 15% fluorine-doped samples reach a maximum critical temperature of 40.2 K for the 50% yttrium substitution. Comparison with literature data indicates that chemical pressure cannot be the only mechanism which tunes drastically both $T_{SDW}$ and $T_c$ in 1111 compounds. Our data suggest that the structural disorder induced by the partial substitution in the La site or by doping could play an important role as well.

## I. INTRODUCTION

Iron-arsenide-based compounds (pnictides) have shown superconductivity (SC) with surprisingly high $T_c$. The first discovered superconductor has been LaFeAsO$_{1-x}$F$_x$ with $T_c$ as high as 26 K.[1] This compound of chemical formula REFeAsO$_x$F$_{1-x}$ (RE being a rare earth) belongs to the so-called "1111" family. After only one month, $T_c$ has doubled thanks to a substitution of the La by different RE elements (Sm, Ce, Nd, Pr, and Gd) yielding an increase up to 52 K with Pr (Ref. 2) and 55 K with Sm.[3] Almost the same high critical temperature has been reported in hole-doped oxygen deficient REFeAsO$_{1-\delta}$ compounds with a maximum critical temperature of 51, 54, and 55 K in Pr, Nd, and Sm systems, respectively.[4,5] Nowadays, $T_c$ seems to have reached its maximum value, (56 K) in the electron-doped Gd$_{1-x}$Th$_x$FeAsO.[6]

The La system presents the lowest $T_c$ within the 1111 family, nearly one half of the maximum value, likely due to the large ionic radius of La. This aspect makes La-1111 one of the best systems to investigate the effects of the external and chemical pressure on $T_c$. By applying an external pressure of 4 GPa to optimally doped LaFeAsO$_{1-x}$F$_x$, $T_c$ has been raised up to 43 K then slowly dropped off to 9 K for larger pressures.[7] F-doped and O-deficient La1111 under external pressure has shown how the increase in $T_c$ is related to doping. LaFeAsO$_{1-\delta}$ under 1.5 GPa (Ref. 8) has shown a superconducting $T_c$ onset of about 50 K, which is the highest record in La-based system.

Also, the role of chemical pressure has been explored by the partial substitution of the RE element in the La$_{1-y}$RE$_y$FeAsO$_{1-\delta}$ compound. $T_c$ up to 43 K has been obtained in the 40% yttrium-substituted compound.[9] In the case

of RE=Sm, a monotonic rise of $T_c$ from 30 K ($y=0$) to ($y=1$) 55 K (Ref. 10) has been reported.

All these experimental results clearly evidence that both the substitution with smaller ions and the application of an external pressure cause lattice shrinkage, even if the mechanisms involved are different. The chemical pressure is isotropic, whereas the external pressure may induce an anisotropic shrinkage because of the pnictide-layered structure. In both cases, a strong correlation between lattice shrinkage and $T_c$ can be established.

The external pressure produces significant effects also on the structural transition and/or spin density wave (SDW) ordering-related temperatures of the parent compound. In a weakly F-doped SmFeAsO sample, a reduction in $T_{SDW}$ with pressure has been observed.[11] A suppression of the SDW with pressure has been put in evidence also in CaFe$_2$As$_2$ (Ref. 12) and in K$_x$Sr$_{1-x}$Fe$_2$As$_2$ (Ref. 13) (122 family). In Ref. 12, it has been argued that the simultaneous increase in $T_c$ and decrease in $T_{SDW}$ with pressure are evidences that pressure induces doping through charge transfer from the charge reservoir block. These aspects have never been considered in systems where the chemical pressure is varied.

In this paper, we investigate the effect of chemical pressure on $T_c$ and $T_{SDW}$ through the partial substitution of the La ions by Y in the pure and 15% F-doped LaFeAsO compounds. Increasing the Y content, the cell parameters reduce monotonically. In the undoped compounds, this shrinking results in a monotone decrease in $T_{SDW}$ down to 120 K, while in the 15% F-doped system the critical temperature increases reaching a maximum of about 40 K for 50% yttrium substitution and then decreases with further increasing yttrium content.

## II. EXPERIMENTAL

### A. Synthesis

The samples of the series $La_{1-y}Y_yFeAsO_{1-x}F_x$ ($y=0$, 0.30, 0.50, and 0.70 and $x=0$ and 0.15) were synthesized at *ambient pressure* by a solid-state reaction method using high-purity (La, Y)As, $Fe_2O_3$, Fe, and $FeF_2$ with a two-step reaction procedure.[14,15] A stoichiometric pellet was pressed and reacted in a welded tantalum crucible closed in quartz ampoules at 1000 °C for 70 h. The pellet was subsequently grinded, mixed, pressed in a new pellet, and annealed with the same procedure at 1250 °C for 25 h. All the handling and manipulation of the samples was carried out in a glovebox, where the working atmosphere was continuously purified to less than 1 ppm $H_2O/O_2$. The use of tantalum crucibles prevented losses of fluorine, the dopant responsible for the superconductivity, even if some consumption of arsenic by tantalum was observed. The final product was a black and hard cylinder, with a density of about 80% of the theoretical value, which has been cut for measurements. The same procedure was also used without success to synthesize the compounds with $y=1$, YFeAsO, and $YFeAsO_{0.85}F_{0.15}$: only a mixture constituted by $Y_2O_3$, YAs, FeAs, and $Fe_2As$ (and YOF in the F-doped sample) was obtained. Probably, in this case, a high-pressure synthesizing method followed by a special rapid quench process would be necessary, as reported by Yang *et al.*[16]

### B. Sample characterization: Structural analysis

Phase identification was performed by the x-ray powder diffraction [(XRPD) PHILIPS PW3020; Bragg-Brentano geometry; Cu $K_\alpha$; range 15–120° $2\theta$; step 0.020°; and sampling time of 10 s]; the crystal structures of the samples were refined in the space group $P4/nmm$-129 (origin choice 2) according to the Rietveld method using the FULLPROF software. By means of a $LaB_6$ standard, an instrumental resolution file was obtained and applied during refinements in order to detect possible microstructural contribution to XRPD peak shape.

Figure 1 shows the Rietveld refinement plot obtained for the sample with nominal composition $(La_{0.70}Y_{0.30})FeAs(O_{0.85}F_{0.15})$, containing (La,Y)As and (La,Y)OF as secondary phases, whose amounts result 6.4% and 8%, respectively.

The effectiveness of the substitution is proved by the monotonic decrease in the $a$- and $c$-lattice parameters obtained from the Rietveld refinement with Y content as shown in Fig. 2. Information on the chemical homogeneity of the samples was obtained analyzing the broadening XRPD lines by means of the Williamson-Hall plot method.[17] Generally, in case size effects are negligible, a straight line passing through the origin have to be observed, whereas the slope provides the lattice strain. When broadening is not isotropic, size and strain effects along some crystallographic directions can be obtained by considering different orders of the same reflection. For solid solutions, the $\Delta d/d$ ($d$: interplanar spacing) term can also have a contribution from chemical fluctuations and inhomogeneities inside the sample because the larger the distribution of lattice parameters the broader the
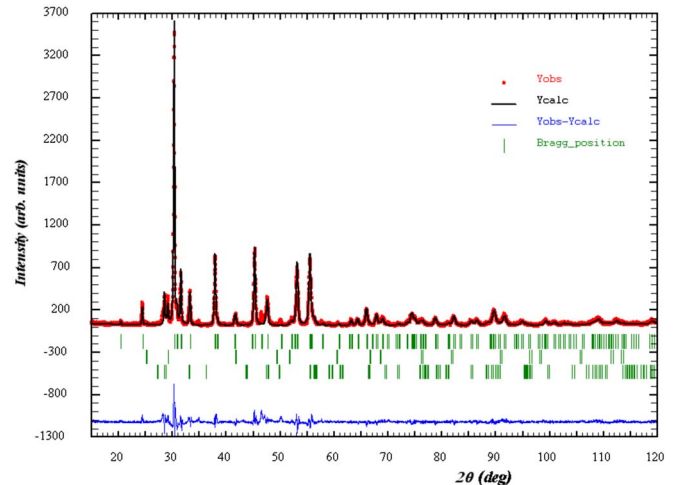


FIG. 1. (Color online) Rietveld refinement plot obtained for the samples with nominal composition $(La_{0.70}Y_{0.30})FeAs(O_{0.85}F_{0.15})$.

peaks. Broadening related to chemical inhomogeneity is generally anisotropic, depending on the symmetry of the crystal system.[18] Williamson-Hall plots for all the F-doped samples (not showed) evidence two main features: (1) size contribution is negligible since a straight line passing through the origin can be traced and (2) broadening related to microstrain and/or chemical fluctuations is isotropic, indicating a good chemical homogeneities of our samples since they crystallize in the tetragonal system.

Figure 2 shows the cell parameters of $La_{1-y}Y_yFeAsO$ and $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ (square symbol) as a function of yttrium nominal content. As expected, in the undoped compounds, starting from the $y=0$ sample ($a=4.033$ Å, $c=8.744$ Å) the effect of the substitution results in a monotonic decrease by 1.8% and 1.7% of $a$- and $c$-lattice parameters, respectively, for the highest yttrium content ($a=3.962$ Å, $c=8.597$ Å). The 15% fluorine doping shows a further shrinkage of about 0.3% of these cell parameters, indicating the covalent character of the intralayer chemical bonding due to the smaller radius of fluorine as compared to the oxygen one.[3]

Substitution at the La site has been earlier reported in oxygen deficient $La_{1-x}Y_xFeAsO_{1-\delta}$ compounds produced by the high-pressure synthesis process:[9] the $a$- and $c$-lattice parameters exhibit a weak decrease, 0.92% and 0.88%, respec-
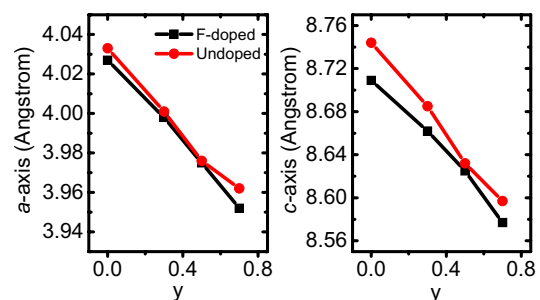


FIG. 2. (Color online) Cell parameters of $La_{1-y}Y_yFeAsO$ (circle symbol) and $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ (square symbol) as a function of yttrium nominal content.

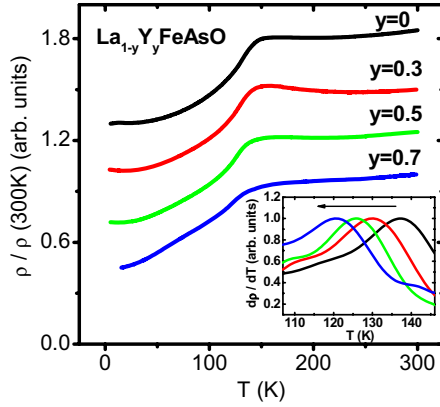FIG. 3. (Color online) $La_{1-y}Y_yFeAsO$ normalized resistivity versus temperature behavior. The inset shows the shift toward low temperatures of the maximum of normalized $d\rho/dT$ with increasing the yttrium content.

tively, for 40% yttrium substitution. With the $y=0.7$ sample, we were able to shrink the axes more than twice, which allows us to investigate the effect of chemical pressure in a more extended range.

### C. Sample characterization: Resistive measurements

Resistive measurements were taken using a standard four-probe technique. In Fig. 3 resistivity versus temperature measurements of the undoped compounds are shown. Data have been normalized to the room-temperature values and shifted for a better visualization.

Upon cooling, $\rho(T)$ of undoped samples presents typical features of the iron-based oxypnictides compounds: a maximum followed by a sharp drop with an inflection point at $T_{drop}$ defined as the maximum of the first derivative $d\rho/dT$. We recall that in LaFeAsO (Refs. 19 and 20) and in PrFeAsO compounds,[21] the maximum of $\rho$ has been attributed to the occurrence of the structural transition, while the maximum of the first derivative to the SDW transition. For the $SmFeAsO_{1-x}F_x$ system, the two transitions seem to coincide.[22]

By increasing the yttrium content, a broadening of the maximum in the $\rho(T)$ is observed up to its disappearance in the case of 70% Y-substituted sample. Furthermore, $T_{drop}$ is shifted to lower temperatures starting from a value of $T_{drop}=138$ K in the LaFeAsO down to 120 K in the 70% Y-substituted compound. In the following, we assume $T_{drop} \equiv T_{SDW}$. In Fig. 4, $\rho(T)/\rho(300$ K$)$ for 15% F-doped compounds are plotted and shifted for better visualization.

The critical temperatures $T_c$ are evaluated by considering the intersection of the two straight lines drawn on $\rho(T)$ data in the normal state just above $T_c$ and its steepest part in the SC state, as reported in Ref. 7. $T_c$ increases with the Y content, reaches a maximum $T_c=40.2$ K for $y=0.5$, and then decreases. All data for undoped and F-doped samples are collected in Fig. 5, which shows the evolution of $T_{SDW}$ and $T_c$ as a function of the yttrium content.

### D. Sample characterization: dc magnetic measurements

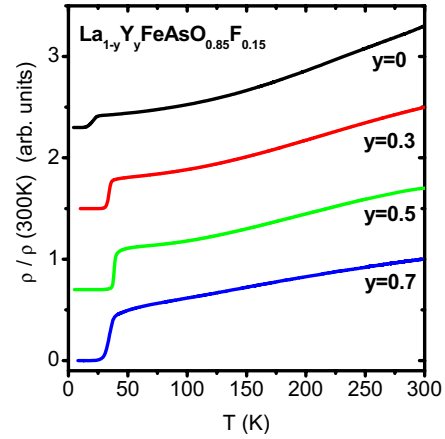dc magnetization was performed in a dc-superconducting quantum interference device(SQUID) magnetometer (mag-

netic properties measurement system, Quantum Design). The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) dc magnetizations ($m$) taken with an applied dc field $\mu_0H=10^{-3}$ T for the $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ compounds are plotted in Fig. 6. The drop in $m(T)$ indicates the onset of the superconductivity.

The shielding values is about $-1$ for the samples with $y=0$, whereas it becomes rather low with increasing yttrium content: 30% for the $y=0.3$ sample and down to 15% for the $y=0.7$ sample. The low shielding values are indicative of bad weak links between grains and of the effect of the penetration depth $\lambda$ ($\sim300$ nm at low temperature[23]) on the shielded grain volume (the mean grain size is about few $\mu$m). The presence of spurious magnetic phases may be inferred also from the positive offset shown by $m(T)$ above the SC transition and from the slight upturn of magnetization at low temperature observed in some curves. $T_c$ values evaluated from magnetization measurements indicated by the black arrows in Fig. 5 are a bit lower than those evaluated by
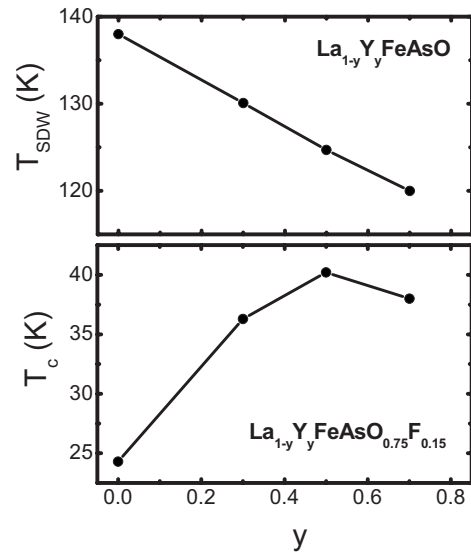


FIG. 4. (Color online) Temperature dependence of the resistivity for $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ compounds.



FIG. 5. Temperature evolution of $T_{SDW}$ and $T_c$ as a function of yttrium content for $La_{1-y}Y_yFeAsO$ and $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ compounds.
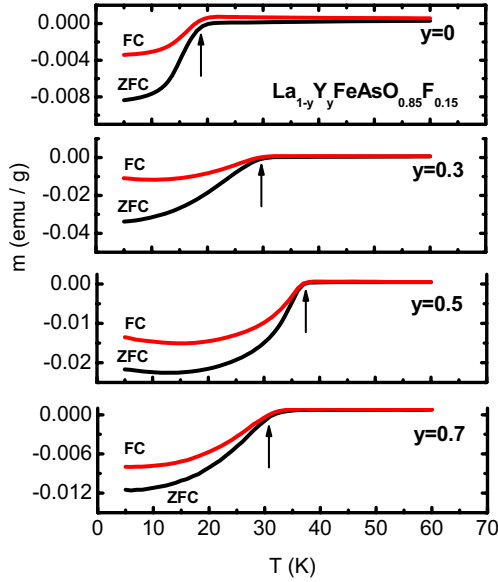
FIG. 6. (Color online) ZFC and FC magnetizations for $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ compounds. The black arrows indicate the critical temperatures $T_c$ evaluated in the same way as the resistivity ones, that is, through the intersection of the lines corresponding to the normal state above $T_c$ and the steepest part of the magnetization in the superconducting one.

the resistivity but present the same behavior as a function of $y$.

### III. DISCUSSION

We have shown that both $T_c$ in $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ samples and $T_{SDW}$ in the parent $La_{1-y}Y_yFeAsO$ samples present a clear dependence on the Y content. Since the lattice parameters monotonically shrink with increasing Y content, the evolution of $T_c$ and $T_{SDW}$ can be discussed as a function of chemical pressure.

Figure 7(a) shows the critical temperatures of the $La_{1-y}Y_yFeAsO_{0.85}F_{0.15}$ series as a function of $a$ axis with data collected from literature. As it was previously noted for oxygen deficient compounds,[9] the literature data of the 1111 family seem to stay into a common line which describes the increase in $T_c$ with the decrease in the lattice parameters, showing a clear indication in favor of the role played by the chemical pressure in increasing $T_c$.

Our 15% F-doped La-Y series, instead—by increasing the chemical pressure—show a peculiar domelike behavior, compressed and shifted in the right-bottom side of the graph in respect to that of the 1111 family with high-$T_c$ rare earth. With decreasing the $a$ axis, $T_c$ increases showing a maximum which is about 40 K for $a=3.975$ nm and then decreases for smaller $a$ axis.

In Fig. 7(b) we plot $T_{SDW}$ of the $La_{1-y}Y_yFeAsO$ series as a function of $a$-lattice parameter with data collected from literature on the 1111 family, with RE=Ce, Pr, Nd, Sm, Gd, and Tb. In all these data, $T_{SDW}$ was estimated by the maximum of $d\rho/dT$. The graph shows two distinct curves which monotonically rise with increasing the $a$ axis. The upper line
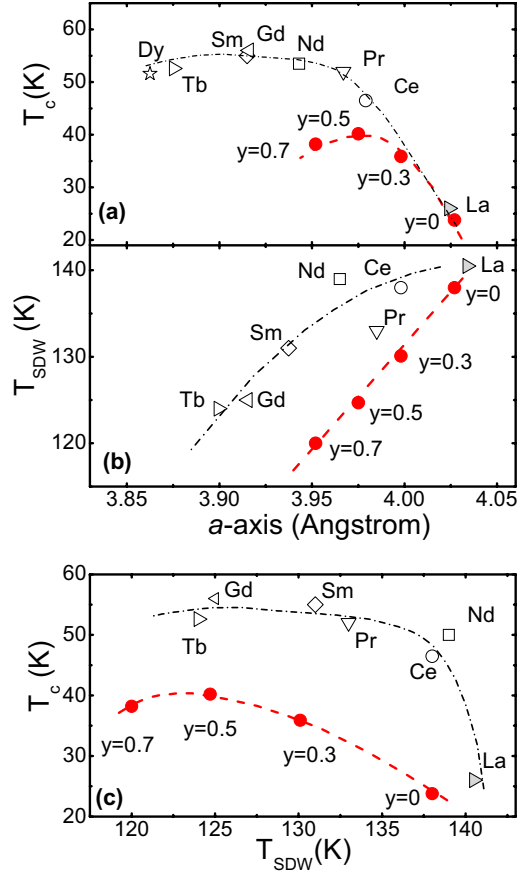


FIG. 7. (Color online) (a) $T_c$ and (b) $T_{SDW}$ vs the $a$ axis, for the $La_{1-y}Y_yFeAsO_{0.75}F_{0.15}$ samples (full circle) in comparison with data collected from literature for 1111 compounds with different rare earths. (c) $T_c$ versus $T_{SDW}$ for La-Y series and other rare earths. The SC samples used for comparison are $LaFeAsO_{0.9}F_{0.1-\delta}$ (Ref. 24), $CeFeAsO_{0.84}F_{0.16}$ (Ref. 25), $PrFeAsO_{0.84}F_{0.16}$ (Ref. 2), $NdFeAsO_{1-\delta}$ (Ref. 5), $SmFeAsO_{0.9}F_{0.1}$ (Ref. 3), $Gd_{0.8}Th_{0.2}FeAsO$ (Ref. 6), $TbFeAsO_{1-\delta}$ (Ref. 26), and $DyFeAsO_{1-\delta}$ (Ref. 26). $T_{SDW}$ data for undoped REFeAsO are, when different data are present for the same compound, the average between the maximum and minimum values reported: La [$T_{SDW}=138$ K (Ref. 19) and $T_{SDW}=143$ K (Ref. 27)]; Ce [$T_{SDW}=136$ K (Ref. 27) and $T_{SDW}=140$ K (Ref. 28)]; Pr [$T_{SDW}=127$ K (Ref. 21) and $T_{SDW}=139$ K (Ref. 27)]; Nd [$T_{SDW}=137$ K (Ref. 29) and $T_{SDW}=141$ K (Ref. 27)]; Sm [$T_{SDW}=131$ K (Ref. 26)]; Gd [$T_{SDW}=125$ K (Ref. 6)]; and Tb [$T_{SDW}=124$ K (Ref. 26)].

contains all the high-$T_c$ rare earths. The lower line contains the La-Y series. This behavior resembles the one reported for $T_{SDW}$ versus external pressure in the 1111 (Ref. 11) and 122 (Refs. 12 and 13) families, confirming the effectiveness of the Y substitution in La site in producing chemical pressure.

The twofold effects of increasing $T_c$ and decreasing $T_{SDW}$ were considered as evidence of doping induced by pressure.[13] Our data cannot exclude that chemical pressure can contribute to doping, but the indication we can draw is that this is a small effect. In fact, in the undoped compound, starting from $y=0$, the $a$ axis is shrunk by 1.8% without observing the occurrence of superconductivity, while the superconductivity occurs after F substitution, which causes a much lower further shrinkage (about 0.3%). Therefore, we

conclude that in the 1111 family, doping with F, as well as the O vacancies, is able to suppress the SDW and favor superconductivity much more effectively than chemical pressure does.

Finally, Fig. 7(c) shows $T_c$ as a function of $T_{SDW}$. Also in this case, a correlation can be found provided that we consider separately the La-Y series and the high-$T_c$ rare-earth series. The graph suggests that smaller $T_{SDW}$ favors higher $T_c$, even with a saturation around 55 and 40 K, in the high-$T_c$ rare earth and in La-Y series, respectively, occurs. This point needs more investigation.

It is interesting to discuss the differences between La and other rare-earths 1111 compounds that emerge from the discussion above. It is evident that the larger ionic radius of La cannot explain these differences because by substituting a certain amount of Y, we can obtain a cell volume smaller than in the case of Ce and Pr and comparable with that of Nd, but $T_c$ values remain smaller.

We should point out that the substitution of La with Y decreases the average lattice parameters, but—locally—this could not be equivalent to the effect exerted by ions with smaller radius. Structural disorder induced by substitution could also be detrimental to superconductivity. Moreover, an important role can also be played by a different kind of doping. By substituting up to 50% of F, $T_c$ does not reach 40 K, while reducing O, $T_c$ over 40 K can be obtained.[8] To better clarify the different effects of doping and chemical pressure, further studies on La-Y series with a different type of doping can be useful.

## IV. CONCLUSIONS

In order to investigate the effect of chemical pressure on normal and superconducting properties of the 1111 compounds, we have synthesized $La_{1-y}Y_yFeAsO_{1-x}F_x$ compound as a function of yttrium content and $x=0$ and 0.15 at ambient pressure. The progressive inclusion of Y is proved by the monotonic decreasing in the lattice parameters as a function of $y$ content. In the undoped compounds, the SDW ordering progressively shifts to lower temperature and superconductivity does not occur. In the 15%-doped samples, $T_c$ progressively grows from 24 to 40 K with increasing $y$ from 0 to 0.5 and then decreases. Similar evolution of $T_{SDW}$ and $T_c$ has been observed as a function of external pressure, indicating that chemical and external pressures play a very similar role.

To emphasize the role of chemical pressure, we have plotted $T_{SDW}$ and $T_c$ as a function of $a$ axis of La-Y series, in comparison with other rare earths. Both $T_{SDW}$ and $T_c$ of La-Y system evolve in similar but distinct way with respect to other high-$T_c$ rare-earths-1111 compounds.

Lattices parameters have been widely varied in the La-Y series obtaining $a$-axis values in between those of Nd and Sm. This indicates that chemical pressure cannot be the only mechanism which tune drastically both $T_{SDW}$ and $T_c$ in 1111 compounds. Our data suggest that the structural disorder induced by the partial substitution in the La site or by doping could play an important role as well.

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