Lattice anomalies in the FeAs$_4$ tetrahedra of the NdFeAsO$_{0.85}$ superconductor that disappear at $T_c$

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Abstract – High-resolution synchrotron X-ray powder diffraction (SXRPD) was used to study the temperature dependence of the oxygen-deficient NdFeAsO$_{0.85}$ superconducting compound. By employing a dense temperature sampling we have managed to reveal unnoticed structural modifications that start around $\sim 180$ K, and disappear at the transition temperature. The data show minor changes of the structural characteristics in the Nd-O charge reservoir layer while in the superconducting Fe-As layer the FeAs$_4$ tetrahedron shows gradual modifications below $\sim 180$ K, which suddenly disappear at $T_c$ strongly indicating a connection with superconductivity.

Introduction. – The discovery of superconductivity in iron-based layered compounds REFeAsO$_{1-x}$F$_x$ (RE = Sm, Nd, Ce, Pr, Gd) belonging to the family of oxypnictides [1] attracted a lot of experimental and theoretical attention. However the mechanism, which induces superconductivity by doping the parent REFeAsO compound, is still controversial. REFeAsO has been found to undergo a structural tetragonal-to-orthorhombic phase transition upon cooling [2–4] and exhibits a spin density wave antiferromagnetic (AF) ordering [2,5–7] closely resembling the cuprates. Both phenomena seem to be suppressed by doping and with the appearance of superconductivity. However in the hole-doped Nd$_{1-x}$Sr$_x$FeAsO superconducting compound the structural phase transition is not suppressed by increasing the Sr$^{2+}$ content [8]. In the oxygen-deficient superconducting compound REFeAsO$_{1-\delta}$ [9] with $T_c$ ranging from 31.2 K for RE = La to 55 K for RE = Sm and $\delta = 0.15$, the tunable oxygen content leads to the occurrence of superconductivity strongly resembling the situation in cuprate superconductors.

Low-temperature Fourier Transform Infrared (FTIR) studies in one of the highest-$T_c$ (53.5 K) pnictides (NdFeAsO$_{0.85}$ [9]) have revealed unexpected spectral modifications and temperature-dependent anomalies for certain modes at $\sim 180$ K [10]. Some marginal evidence of inflection points near $T_c$ in the temperature dependence of the bond angle $\alpha$$_{As-Fe-As}$ and bond length $d$$_{Fe-As}$ has been recently reported for a NdFeAsO$_{0.85}$ sample [11]. In addition a femtosecond spectroscopy study of a single crystal SmFeAsO$_{0.8}$F$_{0.2}$ superconducting sample revealed the presence of a pseudogaplike feature with an onset above 180 K [12]. Moreover, in the non-superconducting LaFeAsO$_{1-x}$F$_x$ a clear lattice anomaly has been detected at $\sim 180$ K that disappears upon AF ordering [13]. Detailed and accurate structural studies as a function of temperature are therefore essential in order to establish a clear picture of any correlation between crystal and electronic structures in the iron-based superconductors.

We present here high-resolution synchrotron powder diffraction results as a function of temperature from the superconducting NdFeAsO$_{0.85}$ system ($T_c = 53.5$ K) [9]. Our data recorded with a dense sampling in the temperature range down to 10K provide clear evidence of subtle lattice distortions that start at $T_{onset} \approx 180$ K and disappear at $T_c$.

Experimental. – We have collected SXRPD data on beamline ID31 at the European Synchrotron Radiation Facility, Grenoble, France. The experimental details are given in the supplementary material. We have obtained high-resolution data from 10 K to 300 K for the NdFeAsO$_{0.85}$ sample along the $a$ and $b$ axes, and the temperature dependence of the $c$ axis. The SXRPD data were collected in a dedicated high-resolution experimental set up [14] using a CuK$_{\alpha}$ ($\lambda = 1.5406$ Å) radiation source with a resolution of 0.05° in 2$\theta$.
Facility (ESRF), Grenoble, France. The experimental set-up is described in detail elsewhere [14]. The short wavelength ($\lambda = 0.39998(5) \text{ Å}$), to reduce absorption, was selected with a double-crystal Si(111) monochromator and calibrated with Si NIST standard. Optimum transmission was achieved by enclosing the finely ground sample in a 0.6 mm diameter borosilicate glass capillary and appropriate spinning of the capillary in the beam ensured for a good powder averaging. An exchange gas continuous liquid-helium flow cryostat with rotat-ensured for a good powder averaging. An exchange sample in a 0.6 mm diameter borosilicate glass capillary transmission was achieved by enclosing the finely ground mator and calibrated with Si NIST standard. Optimum was selected with a double-crystal Si(111) monochro-
in fig. 1. Table 1 shows the structural parameters at phase transition down to 10 K, as shown in the inset
would be the sign of a tetragonal-orthorhombic (T-O) splitting or broadening of the 110 reflection profilesthat 
Rietveld refinement. The high-resolution data reveal no a0tions for NdFeAsO$_{0.85}$. The two lower rows of bars indicate 
the Bragg peak positions of the impurity phases FeAs and Nd$_2$O$_3$, respectively. The inset shows the profiles of the 110 reflection at different temperatures. Intensities are scaled to the most intense line in the spectrum $I_{\text{max}}$ and peaks are shifted to be superimposed.

Results and discussion. – Figure 1 shows the diffraction pattern at 10 K together with the result of the Rietveld refinement. The high-resolution data reveal no splitting or broadening of the 110 reflection profiles that would be the sign of a tetragonal-orthorhombic (T-O) phase transition down to 10 K, as shown in the inset in fig. 1. Table 1 shows the structural parameters at different temperatures obtained from the Rietveld refinement of the high-statistics patterns. The position of the As atom does not change in the whole temperature range examined. The fractional coordinate of the Nd atom along the c-axis remains constant down to 140 K, it jumps to a higher value within 140 K–60 K, indicating that the Nd atom shifts closer to the superconducting Fe-As layer, and then it remains practically constant to the lowest temperature studied. The thermodiffractograms between the characteristic temperatures have been analyzed using both the Rietveld and the Le Bail (whole-powder pattern decomposition method not based on the structural model) method.

Minor impurity peaks were excluded from the refinement. The Rietveld analysis has been performed combined with the high-statistics data, i.e., the atomic positions and the atomic displacement factors $U_{\text{iso}}$ of NdFeAsO$_{0.85}$. Oxygen occupancy has been fixed to the nominal value, justified by the agreement of the Nd-As bond length value to that obtained from a neutron diffraction study in a series of variable oxygen stoichiometry NdFeAsO$_{1-y}$ samples [17]. The refinements take into account small amounts of the impurity phases FeAs ($5 \pm 0.9$ wt%) and Nd$_2$O$_3$ ($1.4 \pm 0.3$ wt%) while a few very weak peaks due to other minor impurity phases ($< 0.1$ wt%) have been excluded. We note that excluding also the peaks of the two main impurity phases does not affect the structural results.

The temperature dependence of the c- and a-axis (fig. 2) reveals two important features: a slope change at $T \sim 180$ K and a subtle anomaly at $T_c$. The lattice of NdFeAsO$_{0.85}$ contracts anisotropically, the relative change being $\Delta a/a = 0.14\%$ and $\Delta c/c = 0.37\%$ from 295 K to 60 K, in agreement with previous reports [11]. The distance between two adjacent Nd and As atoms that reflects the spacing between the charge reservoir Nd-O

Fig. 1: (Colour on-line) Experimental (circles), calculated (continuous line) SXRPD patterns and their difference (bottom line) at $T = 10$ K. Bars indicate the theoretical Bragg peak positions for NdFeAsO$_{0.85}$. The two lower rows of bars indicate the Bragg peak positions of the impurity phases FeAs and Nd$_2$O$_3$, respectively. The inset shows the profiles of the 110 reflection at different temperatures. Intensities are scaled to the most intense line in the spectrum $I_{\text{max}}$ and peaks are shifted to be superimposed.
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Table 1: Rietveld refinements of synchrotron diffraction data for NdFeAsO$_{0.85}$ at different temperatures. The space group is $P4/nmm$ with Nd on $2c(\tfrac{1}{4}, \tfrac{1}{4}, z)$, Fe on $2b(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{2})$, As on $2a(\tfrac{1}{4}, \tfrac{1}{4}, 0)$, O on $2a(\tfrac{1}{4}, \tfrac{1}{4}, 0)$.

|    | $T = 10$ K | $T = 50$ K | $T = 60$ K | $T = 140$ K | $T = 160$ K | $T = 180$ K |
|----|------------|------------|------------|------------|------------|------------|
| Nd | $z$        | 0.14381(6) | 0.14383(7) | 0.14385(6) | 0.14356(6) | 0.14363(7) | 0.14364(7) |
|    | $U_{iso}$ ($\times 100 \AA^2$) | 0.144(6) | 0.131(7) | 0.145(6) | 0.279(7) | 0.314(8) | 0.293(8) |
| Fe | $z$        | 0.18(2) | 0.16(2) | 0.26(2) | 0.39(3) | 0.39(3) | 0.40(3) |
|    | $U_{iso}$ ($\times 100 \AA^2$) | 0.6586(1) | 0.6586(1) | 0.6584(1) | 0.6584(1) | 0.6586(1) | 0.6587(1) |
| As | $z$        | 0.6586(1) | 0.6586(1) | 0.6584(1) | 0.6584(1) | 0.6586(1) | 0.6587(1) |
|    | $U_{iso}$ ($\times 100 \AA^2$) | 0.18(1) | 0.16(2) | 0.26(1) | 0.38(1) | 0.40(2) | 0.40(1) |
| O  | $z$        | 3.94999(1) | 3.94999(1) | 3.95000(1) | 3.95116(1) | 3.95160(1) | 3.95226(1) |
|    | $U_{iso}$ ($\times 100 \AA^2$) | 0.194(1) | 0.1410 | 0.1357 | 0.1183 | 0.1209 | 0.1322 |
| $a$ | (Å)        | 8.50360(4) | 8.50479(4) | 8.50467(4) | 8.51228(5) | 8.51525(5) | 8.51899(5) |
| $c$ | (Å)        | 1.2(2) | 1.6(3) | 1.7(2) | 1.5(2) | 1.4(2) | 1.4(2) |
| $R_{wp}$ | | 0.1094 | 0.1410 | 0.1357 | 0.1183 | 0.1209 | 0.1322 |
| $R_{F^2}$ | | 0.0951 | 0.1050 | 0.0817 | 0.884 | 0.0807 | 0.949 |

Fig. 2: (Colour on-line) The dependence of the $c$- and $a$-axis on temperature. Full circles: high-statistics scans. Open triangles: thermodiffractograms. Errors are smaller than symbols.

and the superconducting Fe-As layer (fig. 3a), decreases from 295 K to 60 K by 0.23% following the reduction of the $c$-axis. The Nd-O bond contracts upon cooling (0.16%) following the contraction of the $a$-axis (fig. 3b), while the Nd-O-Nd bond angle exhibits only marginal changes with temperature (fig. 3c). On the contrary, the Fe-As bond length in the superconducting layer exhibits a bigger change (0.24%) comparable to that of the $c$-axis (fig. 4a). The tetrahedral bond angle $\alpha_{As-Fe-As}$ (fig. 4b) is increasing while $\beta_{As-Fe-As}$ (fig. 4c) is decreasing, indicating an increase of tetrahedral distortion with decreasing temperature. The FeAs$_4$ coordination tetrahedron is distorted from the ideal symmetry. Robinson et al. [18] have found that a quantitative measure of the distortion in such a case is the variance of the tetrahedral angle expressed as $\sigma^2 = \sum_{i=1}^{6} (\theta_i - 109.47^\circ)^2/5$, where $\theta_i$ are the bond angles of the distorted tetrahedron and 109.47$^\circ$ the corresponding one in an ideal tetrahedron. Figure 5a shows the distortion of the Fe coordination tetrahedron and fig. 5b presents the temperature evolution of the volume [19] of the FeAs$_4$ tetrahedra in comparison to that of the cell volume both normalized to their values at 295 K.

The temperature evolution of all structural features (figs. 2–5) reveals anomalies at characteristic temperatures. Specifically, at $T_{onset} \sim 180$ K a change of slope is evident in the lattice constants (fig. 2), the inter-layer Nd-As distance (fig. 3a), the intra-layer Nd-O bond length (fig. 3b) and angle (fig. 3c), as well as in the geometrical characteristics of the FeAs$_4$ tetrahedra (figs. 4, 5). This change is much more pronounced in the superconducting Fe-As layer. Furthermore, around $T_I \sim 135$ K, a modification in the temperature dependence is evidenced for all bond length characteristics (figs. 3–5). It looks
like a new order parameter coupled to the lattice and mostly to the Fe-As tetrahedra sets in at $T_{\text{onset}}$ which is completed at $T_c$ (figs. 4, 5). At $T_c$ the Fe-As bond length and the distortion of the FeAs$_4$ tetrahedra exhibit a sudden change (figs. 4, 5) while the Nd-O bond length and angle values saturate (fig. 3). The modifications around $T_c$ are not so pronounced in the charge reservoir planes being less sensitive to changes with temperature. The structural data indicate a bigger effect in the superconducting Fe-As planes. The relative contraction of the FeAs$_4$ volume deviates in a profound way from that of the unit cell below $T_{\text{onset}}$ where the angle distortion is also modified. Crossing $T_c$ the anomalies are obviously reduced (fig. 5).

The lattice distortions appear below $\sim 180$ K where certain IR modes exhibit an anomalous behavior in the same compound [10]. The non-superconducting undoped NdFeAsO compound is known to exhibit a tetragonal to orthorhombic phase transition that starts at 150 K [4], and a magnetic ordering of the iron spins below $\sim 141$ K [7]. One could assume that the lattice anomaly observed in the region 180 K–$T_c$ originates from a T-O structural phase transition because such a phase transition can be traced in other superconducting oxypnictides [3,8]. However our high-resolution diffraction data (inset in fig. 1) do not support such possibility. On the other hand, the iron spins could order antiferromagnetically along the $c$-axis at $\sim 141$ K [7], but this phase should be absent in the optimally doped compound, though it may be present at low doping levels [20,21]. The assumption of two chemically separated phases cannot be justified from the XRD results since no splitting or broadening of the XRD peaks was observed. However, a mesoscopic phase separation cannot be excluded, at least in the underdoped pnictides [21]. The observation of similar lattice distortions that start below $\sim 180$ K and relaxes at $T_N$ in the non-superconducting LaFeAsO$_{1-x}$F$_x$ [13] and the appearance of a new photo-induced reflectivity component in the superconducting SmFeAsO$_{0.8}$F$_{0.2}$ [12] point to a lattice distortion effect of common origin in all these pnictides. But while in the non-superconducting compound with the AF ordering the effect disappears at $T_N$, in the photo-induced reflectivity results that probe the electronic states the component remains into the superconducting state, and in our structural data of superconducting compound the lattice distortions are relaxed at $T_c$. It appears that another order parameter, which is common to all compounds sets-in around $T_{\text{onset}}$ and affects spin, lattice, and electronic states.

Based on the Fe-As$_4$ angle modifications (fig. 5a) one could assume local distortions that involve orbital ordering in the Fe planes. Martinelli et al. [22] have proposed that the structural transition could originate by this distortion that brings a similarity of the oxypnictide systems to the manganites. At $T_{\text{onset}}$ both the volume and the distortion of the FeAs$_4$ tetrahedra show an anomaly that saturates at $T_1$ and disappears below $T_c$. The direct effect on the lattice and more precisely the anomalous contraction of the volume of the FeAs$_4$ tetrahedra (fig. 5b) and the increase of their distortion indicates a polaronic mechanism. In such a case, the polarons should start been formed around 180 K. In the undoped compound the polarons could be

![Fig. 4: (Colour on-line) Temperature evolution of the intra-layer Fe-As bond length (a) and Fe-As-Fe angles (b) and (c). Full circles: high-statistics scans with esds. Open triangles: thermodiffractograms with error bars calculated on the basis of error propagation from the corresponding errors of lattice constants and atomic positions.](image1)

![Fig. 5: (Colour on-line) Temperature evolution of (a) the tetrahedral distortion (angle variance), (b) the normalized volumes of FeAs$_4$ (circles and triangles) and unit cell (squares and crosses) to their values at 295 K. Full circles: high-statistics scans with esds. Open triangles: thermodiffractograms with error bars calculated on the basis of error propagation from the corresponding errors of lattice constants and atomic positions.](image2)
related with the AF ordering [13]. In the presence of carriers, the AF ordering is suppressed and the instability remains down to $T_c$ (fig. 5b). The return of the volume of the FeAs tetrahedron (Fe-As bond length) below $T_c$ to the anticipated value from the high-temperature data could be due to the delocalization of the polarons in the superconducting phase. Whatever happens our data show that there are modifications of the $c$-axis at $T_{\text{max}}$ and $T_c$ (fig. 2), and indicate that the lattice effects occur mainly within the FeAs tetrahedra and are related with the carriers and possibly with superconductivity. Anomalies observed at similar temperatures indicate that this might be a general feature of these compounds and reserve further investigation on all pnictides.

In conclusion, the high-resolution synchrotron diffraction data collected with dense sampling in the temperature range 10–295 K revealed the presence of subtle lattice anomalies, which coincide with those in the IR modes at $\sim 180$ K and disappear at the critical temperature. These lattice anomalies, apparently not connected with a structural phase transition, are more evident in the superconducting Fe-As planes consisting of a distortion and contraction of the FeAs tetrahedra and a reduction of the Nd-As distance indicating charge transfer. The disappearance of the anomaly across $T_c$ points to a connection to superconductivity.

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