Effect of Structural Parameters on Superconductivity in Fluorine-Free LnFeAsO$_{1-y}$ (Ln=La,Nd)

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The crystal structure of LnFeAsO$_{1-y}$ (Ln = La, Nd) has been studied by the powder neutron diffraction technique. The superconducting phase diagram of NdFeAsO$_{1-y}$ is established as a function of oxygen content which is determined by Rietveld refinement. The small As-Fe bond length suggests that As and Fe atoms are connected covalently. FeAs$_4$-tetrahedrons transform toward a regular shape with increasing oxygen deficiency. Superconducting transition temperatures seem to attain maximum values for regular FeAs$_4$-tetrahedrons.

KEYWORDS: oxypnictides, superconductivity, powder neutron diffraction, crystal structure analysis

The recent discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ with a transition temperature of $T_c=26$ K has triggered an intense search for related new superconductors.$^1$ Immediately, it was found that $T_c$ increases up to 55 K by replacing La with Sm atoms.$^2$ This is the highest $T_c$ besides that in high-$T_c$ cuprates rendering oxypnictides a promising new class of superconductors.

Because the $T_c$ of the oxypnictide superconductors is very high, it may be difficult to explain the formation of Cooper pairs with the conventional BCS theory. Replacing As by the lighter P results in a strong suppression of the $T_c$ in LaFePO$_{1-x}$F$_x$,$^3$ whose origin also needs to be explained. To elucidate the superconducting mechanism, information about the crystal structure of these materials is very important.

The parent compounds of LnFeAsO (Ln = lanthanide) exhibit a tetragonal structure with the space group P4/nmm at room temperature$^4$ (Fig. 1). Characteristically, LnO and FeAs layers are stacked alternately. Fe atoms are in a four-fold coordination forming a FeAs$_4$-tetrahedron. Upon doping, LnO layers provide carriers to FeAs layers where superconductivity is expected to be induced. The function of the layers appears clearly separated similarly to high-$T_c$ cuprates.

Very recently, it has been reported that the fluorine-free samples LnFeAsO$_{1-y}$ show superconductivity with a maximum $T_c$ of 55 K, as well.$^5,6$ Based on the nominal composition, superconductivity appears to be induced in a wide range of oxygen deficiencies, $0.3 \leq y \leq 0.8$. Since the oxygen deficiency is huge, the crystal structure could be significantly modified compared with that of the parent LnFeAsO compounds. Furthermore, one may doubt that the real oxygen deficiency is as large as the nominal values. Neutron diffraction measurements on the LnFeAsO$_{1-y}$ samples are required to confirm the crystal structure as well as the oxygen content. In this study, we report the relationship between superconductivity and crystal structure in LnFeAsO$_{1-y}$ compounds.

Polycrystalline samples of LnFeAsO$_{1-y}$ (Ln=La,Nd) were synthesized at high pressure and high temperature using a cubic-anvil high-pressure apparatus. Details of synthesis method are given in ref. 5. The nominal oxygen deficiencies at the start of the synthesis was $y=0.15$, 0.20, 0.40, and 0.30 in the NdFeAsO$_{1-y}$ samples labeled 1, 2, 3, and 4. For a LaFeAsO$_{1-y}$ sample, the nominal content is $y=0.40$ (sample 5). The oxygen composition of all the samples was determined by the present Rietveld analysis, and we found that it largely shifts towards higher oxidation (see Table 1). The amount of samples used was about 0.5 g for each composition.

The $T_c$ of the LnFeAsO$_{1-y}$ (Ln=La,Nd) samples was measured using a SQUID magnetometer under a magnetic field of 5 Oe after zero field cooling from sufficiently above $T_c$ (Fig. 2). The oxygen deficiency $y$ indicated in Fig. 2 corresponds to that obtained from the Rietveld analysis of the neutron diffraction patterns. The $T_c$ val-
LaAs, NdAs, FeAs, La and NdF eAsO 3 structures.

![Figure 3](image)

Fig. 2. Shielding signals of LnF eAsO 3 measured under a magnetic field of H = 5 Oe. y was determined by Rietveld refinement. The higher values in the normal states of LaF eAsO 3 (y = 0.12) and NdF eAsO 3 (y = 0.14, 0.17) could be due to slight impurities of iron compounds.

![Figure 3](image)

Fig. 3. Typical observed (crosses) and calculated (solid lines) neutron powder diffraction patterns of NdF eAsO 3. Vertical bars show the calculated positions of nuclear Bragg reflections. The solid lines shown at the bottom of the figure indicate the differences between observations and calculations.

Table 1. Atomic parameters of LnF eAsO 3−y (space group P4/nmm) determined by Rietveld refinements of neutron powder diffraction data. B is the isotropic atomic displacement parameter.

| Atom site | occ. | x   | y   | z   | B (Å²) |
|-----------|------|-----|-----|-----|--------|
| (a) sample 1 (non-super) | T = R.T. | a = 3.9666(7)Å, c = 8.5699(2)Å, R W P = 2.98 % | Nd 2c | 1 | 1/4 | 1/4 | 0.1390(2) | 0.46(4) |
| Fe 2b | 1 | 3/4 | 1/4 | 0.5 | 0.57(4) |
| As 2c | 1 | 1/4 | 1/4 | 0.6571(3) | 0.50(5) |
| O 2a | 0.95(1) | 3/4 | 1/4 | 0 | 0.40(8) |
| (b) sample 2 (Tc = 35 K) | T = R.T. | a = 3.9594(6)Å, c = 8.5550(2)Å, R W P = 2.66 % | Nd 2c | 1 | 1/4 | 1/4 | 0.1413(2) | 0.34(3) |
| Fe 2b | 1 | 3/4 | 1/4 | 0.5 | 0.42(3) |
| As 2c | 1 | 1/4 | 1/4 | 0.6586(3) | 0.53(4) |
| O 2a | 0.920(9) | 3/4 | 1/4 | 0 | 0.67(7) |
| (c) sample 3 (Tc = 44 K) | T = R.T. | a = 3.95365(7)Å, c = 8.5851(2)Å, R W P = 3.25 % | Nd 2c | 1 | 1/4 | 1/4 | 0.129(3) | 0.23(4) |
| Fe 2b | 1 | 3/4 | 1/4 | 0.5 | 0.37(4) |
| As 2c | 1 | 1/4 | 1/4 | 0.6587(3) | 0.39(5) |
| O 2a | 0.86(1) | 3/4 | 1/4 | 0 | 0.32(8) |
| (d) sample 4 (Tc = 51 K) | T = R.T. | a = 3.94755(7)Å, c = 8.5446(2)Å, R W P = 2.84 % | Nd 2c | 1 | 1/4 | 1/4 | 0.1440(3) | 0.42(4) |
| Fe 2b | 1 | 3/4 | 1/4 | 0.5 | 0.40(3) |
| As 2c | 1 | 1/4 | 1/4 | 0.6600(3) | 0.41(5) |
| O 2a | 0.83(1) | 3/4 | 1/4 | 0 | 0.66(8) |
| (e) sample 5 (Tc = 51 K) | T = 10 K | a = 3.9423(1)Å, c = 8.5120(3)Å, R W P = 4.07 % | Nd 2c | 1 | 1/4 | 1/4 | 0.1343(3) | 0.46(6) |
| Fe 2b | 1 | 3/4 | 1/4 | 0.5 | 0.49(5) |
| As 2c | 1 | 1/4 | 1/4 | 0.6624(4) | 0.36(6) |
| O 2a | 0.83 | 3/4 | 1/4 | 0 | 0.48(9) |
| (f) sample 5 (Tc = 28 K) | T = R.T. | a = 4.02291(8)Å, c = 8.7121(2)Å, R W P = 3.87 % | La 2c | 1 | 1/4 | 1/4 | 0.1453(3) | 0.38(5) |
| Fe 2b | 1 | 3/4 | 1/4 | 0.5 | 0.27(4) |
| As 2c | 1 | 1/4 | 1/4 | 0.6527(4) | 0.41(6) |
| O 2a | 0.88(1) | 3/4 | 1/4 | 0 | 0.54(9) |

The superconducting phase diagram of NdFeAsO 3−y versus the oxygen deficiency y determined by Rietveld analysis is shown in Fig. 4. The superconductivity ap-
pears above $y = 0.05$ and attains a maximum $T_c$ value for NdFeAsO$_{1-y}$ compounds around $y = 0.17$. The phase diagram is similar to that of the recently reported fluorine-doped NdFeAsO$_{1-y}$F$_x$ which suggests an equivalent carrier doping level when the $y$ and $x$ values are the same, although the amount of induced carriers should be two times larger for oxygen deficiency.

The selected crystal structural parameters obtained from the Rietveld analysis are shown in Fig. 5. For the non-doped LaFeAsO, the parameters were extracted from the literature, which is consistent with ref. 11. Ln-O bond length increases with increasing oxygen deficiency at the same rate in LaFeAsO$_{1-y}$ and NdFeAsO$_{1-y}$, possibly owing to the decrease in the number of electrons in the O-planes. The bond lengths may be analyzed by the bond-valence-sum (BVS) formalism, in which each bond with a distance $r$ contributes a valence $v = \exp\left[\frac{(d-r)}{d_0}\right]$ with $d$ as an empirical parameter. In the non-superconducting NdFeAsO$_{0.95}$, the four Nd-O bonds contribute 2.235 to the Nd-BVS after correction for the incomplete oxygen occupation. In contrast, the four Nd-As bonds, which are significantly longer, contribute only 0.870 to the Nd-BVS which demonstrates the very anisotropic bonding of the Nd coordination. The total Nd-BVS is 3.104 in good agreement with the expected Nd valency. The increase in Ln-O bond length with doping strongly reduces the Nd-O contribution to the Nd-BVS to 1.888 for $y=0.17$. This reduction is only partially compensated through the pronounced shrinking of Nd-As distance with doping. For $y=0.17$, the Nd-As bonds contribute 0.994 to the Nd-BVS resulting in a total Nd-BVS value of 2.882, which is still close to the expected value. In contrast, the BVS at the Fe site is doping-independent and always far above the value expected for an ionic picture; Fe-BVS=3.522 for $y=0.05$ and 3.485 for $y=0.17$. The enhanced BVS directly indicates that Fe-As bonds are too short compared with an ionic picture and strongly suggests a covalent bonding similar to the cuprates.

The La and Nd series differ in doping dependence of the thickness of the FeAs layer, which is determined by the distance between the As sites and the plane through the Fe sites. This As-Fe$_{\text{plane}}$ distance increases more rapidly in the Nd-based compounds than in the La-based compounds. Related to this, the As-Fe$_{\text{As}}$ bond angles of the Nd-based compounds vary more rapidly with increasing oxygen deficiency approaching a regular FeAs$_4$ tetrahedron in which $\alpha$ and $\beta$ are 109.47°. Also upon cooling, the FeAs$_4$-tetrahedrons become more regular.

The relationship between $T_c$ and FeAs$_4$-tetrahedral distortion is shown in Fig. 6. The tetrahedral distortion is represented by the As-Fe$_{\text{As}}$ bond angle. Clearly, $T_c$ increases as the FeAs$_4$ coordination becomes a regular tetrahedron. This suggests that the maximum $T_c$ values are attained when the FeAs$_4$-lattices form a regular...
tetrahedron. This tendency could not change by lowering temperature, since they become closer to a regular tetrahedron at $T = 10$ K for the sample showing the highest $T_c$. To confirm this idea, we show in Fig. 7 As-Fe-As bond angle as a function of $T_c$ in various pnictide superconductors.\(^1\)\(^-\)\(^3\),\(^\text{6,10,15-27}\) The parameters of the samples showing almost maximum $T_c$ in each system are selected. The vertical dashed line indicates the bond angle of a regular tetrahedron ($\alpha = 109.47^\circ$).

In summary, we have studied the crystal structure of (La,Nd)FeAsO$_{1-y}$ by the neutron diffraction technique. Rietveld analysis revealed that the real oxygen content is largely above the nominal composition. We present the superconducting phase diagram of NdFeAsO$_{1-y}$ against the actual oxygen content. FeAs$_4$-lattices were transformed toward a regular tetrahedron accompanied by an increase in $T_c$ with increasing oxygen deficiency $y$. It seems that $T_c$ becomes maximum when the FeAs$_4$-lattices form a regular tetrahedron.

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