Magnetic order close to superconductivity in the iron-based layered LaO$_{1-x}$F$_x$FeAs systems

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Following the discovery of long-range antiferromagnetic order in the parent compounds of high-transition-temperature (high-$T_c$) copper oxides$^{6,13}$, there have been efforts to understand the role of magnetism in the superconductivity that occurs when mobile 'electrons' or 'holes' are doped into the antiferromagnetic parent compounds. Superconductivity in the newly discovered rare-earth iron-based oxide systems ROFeAs (R, rare-earth metal) also arises from either electron or hole doping of their non-superconducting parent compounds. The parent material LaOFeAs is metallic but shows anomalies near 150 K in both resistivity and d.c. magnetic susceptibility$^5$. Although optical conductivity and theoretical calculations suggest that LaOFeAs exhibits a spin-density-wave (SDW) instability that is suppressed by doping with electrons to induce superconductivity$^6$, there has been no direct evidence of SDW order. Here we report neutron-scattering experiments that demonstrate that LaOFeAs undergoes an abrupt structural distortion below 155 K, changing the symmetry from tetragonal (space group $P4/nmm$) to monoclinic (space group $P112/n$) at low temperatures, and then, at $\sim$137 K, develops long-range SDW-type antiferromagnetic order with a small moment but simple magnetic structure. Doping the system with fluorine suppresses both the magnetic order and the structural distortion in favour of superconductivity. Therefore, like high-$T_c$ copper oxides, the superconducting regime in these iron-based materials occurs in close proximity to a long-range-ordered antiferromagnetic ground state.

The recent discovery of superconductivity in RO$_{1-x}$F$_x$FeAs (refs 3–7) has generated enormous interest because these materials are the first non-copper oxide superconductors with $T_c$s exceeding 50 K. Because these superconductors are derived by doping their non-superconducting parent compounds, it is natural to wonder what the ground states of the parent compounds are. It has been argued theoretically that non-superconducting LaOFeAs is either a non-magnetic metal near a magnetic (antiferromagnetic and/or ferromagnetic) instability$^{10–12}$ or an antiferromagnetic semimetal$^{13–15}$. As a function of temperature, the resistivity of LaOFeAs shows a clear drop around 150 K before increasing again below 50 K (refs 3, 9). The d.c. magnetic susceptibility also has a small anomaly near 150 K. From optical measurements and theoretical calculations$^6$, it has been argued that LaOFeAs has an antiferromagnetic SDW instability below 150 K and that superconductivity in these materials arises from the suppression of this SDW order.

We used neutron diffraction to study the structural and magnetic order in polycrystalline, non-superconducting LaOFeAs and superconducting LaO$_{1-x}$F$_x$FeAs with $x = 0.08$ ($T_c = 26$ K). Our experiments were carried out on the BT-1 powder diffractometer and the BT-7 thermal triple-axis spectrometer at the NIST Center for Neutron Research, and on the HB-1A triple-axis spectrometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory. Figure 1a shows the high-resolution neutron powder diffraction data obtained using the BT-1 diffractometer and our refinements for non-superconducting LaOFeAs at 170 K. Consistent with earlier reports$^{3–9}$, we find that the crystal structure belongs to the tetragonal space group $P4/nmm$, with atomic positions given in Table 1. On cooling the sample to 4 K, the (2, 2, 0) reflection that has a single peak at 170 K (Fig. 1a, inset) is split into two peaks (Fig. 1b, inset). This suggests that a structural phase transition has occurred. For comparison, we note that the (2, 2, 0) peak remains a single peak even at 10 K (Fig. 1c inset) for superconducting LaO$_{0.92}$F$_{0.08}$FeAs. To understand the low-temperature structural distortion in LaOFeAs, we carried out refinement using the neutron data and found that the structure in fact becomes monoclinic and belongs to space group $P112/n$ (see Supplementary Information). Table 2 summarizes the low-temperature lattice parameters and atomic positions for LaOFeAs. Table 3 summarizes the lattice parameters and atomic positions for superconducting LaO$_{0.92}$F$_{0.08}$FeAs at 10 K, 35 K, and 170 K. Figure 1d shows the LaOFeAs structure.

To see if the newly observed structural transition is related to the $\sim 150$ K resistivity anomaly, we carried out detailed temperature-dependent measurements of the (2, 2, 0) reflection and found that there is an abrupt splitting of the (2, 2, 0) peak at 155 K (Fig. 2). The peak intensity also shows a clear kink at 155 K. These results indicate that the non-superconducting system has a structural phase transition, and this phase transition is associated with the observed resistivity$^7$ and specific heat anomalies$^8$. Because a similar splitting of the (2, 2, 0) peak is absent in superconducting LaO$_{0.92}$F$_{0.08}$FeAs (Fig. 1c), we can safely assume that this transition is suppressed with the

Table 1 | Properties of LaOFeAs at 175 K

| Atom | Site | $x$ | $y$ | $z$ | $d(\text{Å})$ |
|------|------|-----|-----|-----|--------|
| La   | 2c   | $\frac{1}{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.1418 (3) |
| Fe   | 2b   | $\frac{1}{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.6507 (4) |
| As   | 2c   | $\frac{1}{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.238 (8) |
| O    | 2a   | $\frac{1}{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.69 (7) |

Table 2 | Selected interatomic distances and angles

| Distance | Value (Å) |
|----------|-----------|
| La–As    | 3.378 (1) |
| Fe–As    | 2.407 (2) |
| La–O     | 2.365 (2) |
| As–Fe–As | 1.0741 (7) |
| Fe–Fe    | 2.8496 (7) |

Space group, $P4/nmm$; $a = 4.03007 (9)$ Å; $c = 8.7368 (2)$ Å; $V = 141.8998 (9)$ Å$^3$. $R_p = 5.24$%, weighted $R_p = 6.62$%, $x^2 = 0.9821$. $^{1}$Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200, USA. $^{2}$Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA. $^{3}$NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, USA. $^{4}$Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742-6393, USA. $^{5}$Tianjin Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, USA. $^{6}$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China. $^{7}$US Department of Energy, Office of Science, Office of Basic Energy Science, Office of Basic Energy Sciences, Washington, DC 20585, USA. $^{8}$Tianjin University, Tianjin 300072, China. $^{9}$International Center for Materials Science, Tsinghua University, Beijing 100084, China.
appearance of superconductivity in LaO$_{1-x}$F$_x$FeAs through doping with fluorine.

It would be interesting to see whether this phase transition in non-superconducting LaOFeAs is indeed associated with SDW order. Figure 3a shows our raw data for LaOFeAs collected on the BT-7 spectrometer at 8 K and 170 K. Inspection of the figure immediately reveals that there are extra peaks in the low-temperature spectrum at wavevector magnitudes $Q = 1.15$, $1.53$ and $2.5\ \text{Å}^{-1}$, which are not

Table 2 | Properties of LaOFeAs at 4 K

| Atom | Site | x  | y  | z   | b(Å$^2$) |
|------|------|----|----|-----|----------|
| La   | 2e   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.1426(3) | 0.54(6) |
| Fe   | 2f   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.5006(12) | 0.16(4) |
| As   | 2e   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.6499(4) | 0.23(7) |
| O    | 2f   | $\frac{1}{4}$ | $\frac{1}{4}$ | -0.0057(17) | 0.69(7) |

Table 3 | Properties of LaO$_{0.92}$F$_{0.08}$FeAs at 10 K (first line), 35 K (second line) and 175 K (third line)

| Atom | Site | x  | y  | z   | b(Å$^2$) |
|------|------|----|----|-----|----------|
| La   | 2c   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.1448(3) | 0.40(5) |
| Fe   | 2b   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.1458(3) | 0.50(5) |
| As   | 2c   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.1446(3) | 0.73(5) |
| O/F  | 2a   | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.6521(4) | 0.41(7) |

Space group, P4/nmm. At 10 K, $a = 4.0202(1)$ Å, $c = 8.70342(2)$ Å, $V = 140.66(1)$ Å$^3$, $R_p = 5.34\%$, weighted $R_w = 6.95\%$, $\chi^2 = 1.028$. At 35 K, $a = 4.0196(1)$ Å, $c = 8.70272(2)$ Å, $V = 140.61(1)$ Å$^3$, $R_p = 5.38\%$, weighted $R_w = 6.96\%$, $\chi^2 = 1.050$. At 175 K, $a = 4.0229(1)$ Å, $c = 8.7142(2)$ Å, $V = 141.03(1)$ Å$^3$, $R_p = 5.30\%$, weighted $R_w = 6.93\%$, $\chi^2 = 0.988$. The small lattice parameter and cell volume differences between 10 K and 35 K data are within the uncertainties of our measurements.

Figure 1 | Temperature dependence of the nuclear structures for LaOFeAs and LaO$_{0.92}$F$_{0.08}$FeAs. We prepared $2\ \text{g}$ each of LaOFeAs and LaO$_{0.92}$F$_{0.08}$FeAs using the method described in ref. 9. The BT-7 diffractometer has a Ge(3, 1, 1) monochromator and an incident beam wavelength of $\lambda = 2.0785$ Å. A, Observed (red crosses) and calculated (green solid line) neutron powder diffraction intensities of LaOFeAs at 175 K using space group $P4/nmm$. The inset shows a single peak of the (2, 2, 0) reflection. Short black vertical lines show the Bragg peak positions. The purple trace indicates the intensity difference between the observed and calculated structures. $\theta$, Diffraction angle. B, The same scan at 4 K, where the (2, 2, 0) reflection is split owing to the monoclinic distortion. The fit was made using space group $P12_1/n$. C, The 10 K scan of superconducting LaO$_{0.92}$F$_{0.08}$FeAs; the space group $P4/nmm$ can describe data at all measured temperatures. D, Crystal structure of LaO$_{1-x}$F$_x$FeAs. For $x = 0$, the compound has the charge-balance configuration La$^{3+}$O$^{2-}$Fe$^{2+}$As$^{5-}$. Electron doping can be achieved by replacing O with F.
present at 170 K. Indexing these peaks (Fig. 3a) indicates that these reflections are indeed directly related to the nuclear structure and are due to magnetic scattering arising from a simple stripe-type antiferromagnetic structure of iron moments with a magnetic cell \(2a_N \times 2b_N \times 2c_N\) (Fig. 4, top-right inset), where \(a_N\), \(b_N\), and \(c_N\) are the nuclear lattice parameters of the unit cell (see Table 1). Figure 3c shows our refinements considering both the magnetic and structural unit cell. Normalizing the magnetic intensity to the nuclear scattering, we find an ordered iron moment of \(0.36(5)\mu_B\) at 8 K (in our results, figures in parentheses indicate uncertainty in the final decimal place; \(\mu_B\) denotes the Bohr magneton). For comparison, Fig. 3b shows the HB-1A spectrometer data for LaOFeAs and La\(_{0.92}\)Fe\(_{0.08}\)As. For non-superconducting LaOFeAs, the temperature difference spectrum (8–170 K) shows a clear peak at \(Q = 1.53\ \text{Å}^{-1}\), which corresponds to the magnetic (1, 0, 3) Bragg peak. This peak is absent from the scan of superconducting La\(_{0.92}\)Fe\(_{0.08}\)As.

To see if the observed magnetic scattering at low temperature in LaOFeAs is indeed associated with the 4K phase transition, we carried out order parameter measurements on the strongest (1, 0, 3) magnetic peak using both the BT-7 and the HB-1A spectrometers. Figure 4 shows the temperature dependence of the square of the ordered magnetic moment (normalized at low temperature), which vanishes at \(\sim 137\ \text{K}\), about \(\sim 18\ \text{K}\) lower than the temperature at which the structural phase transition occurs (Fig. 2). Surprisingly, the magnetic order is established at lower temperatures than the structural distortion, much as spin ordering is established after the lattice distortion above the \(T_N\) temperature. This supports the prediction of a structural distortion, not SDW ordering as originally suggested\(^9\). The top-right inset in Fig. 4 shows the magnetic structure we determined for the system.

To summarize, we have discovered that the parent compound of the iron-based superconductors is a long-range-ordered antiferromagnet with a simple stripe-type antiferromagnetic structure within the plane that is doubled along the \(c\) axis (Fig. 4, top-right inset). There is a structural phase transition before the antiferromagnetic phase transition that changes the structure from space group \(P4/mnm\) to space group \(P12_1/n\) at low temperature. The magnetic structure is consistent with the theoretical prediction\(^7\), but the moment of \(0.36(5)\mu_B\) per iron atom that we observe at 8 K is much smaller than the predicted value of \(\sim 2.3\mu_B\) per iron atom (refs 13, 14). The presence of magnetic frustration might induce the reduced ordered moment\(^7\). The disappearance of the static antiferromagnetic order and lattice distortion in the doped superconducting materials suggests that the underlying physical properties of this class of superconductors may have important similarities to the high-\(T_c\) copper oxides. In any case, we are confident that this new class of materials will open new avenues of research regardless of the origin of the electron pairing and superconductivity.

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**Figure 2** | Temperature dependence of the (2, 2, 0) nuclear reflection indicative of a structural phase transition at \(\sim 155\ \text{K}\) in LaOFeAs. Peak intensities at the (2, 2, 0)\(_T\) (tetragonal) reflection (open symbols, right-hand scale) and positions of the (2, 2, 0)\(_T\), (−2, 2, 0)\(_M\) (monoclinic) and (2, 2, 0)\(_M\) peaks (solid symbols, left-hand scale) as a function of temperature on cooling. A structural transition from tetragonal symmetry \(P4/nmm\) to monoclinic symmetry \(P12_1/n\) occurs at \(\sim 155\ \text{K}\). Error bars, 1 s.d. Inset shows the (2, 2, 0)\(_T\) reflection at 175 K and the (−2, 2, 0)\(_M\) and (2, 2, 0)\(_M\) reflections at 4 K.

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**Figure 3** | Temperature dependence of the magnetic scattering for LaOFeAs and La\(_{0.92}\)Fe\(_{0.08}\)As. a, LaOFeAs data clearly showing (marked) magnetic peaks at 8 K that disappear at 170 K, counting 1 min per point. b, The temperature difference spectra (8–170 K) measured using the HB-1A spectrometer for LaOFeAs (red) and La\(_{0.92}\)Fe\(_{0.08}\)As (blue), counting 4 min per point. The magnetic (1, 0, 3) peak is missing from the La\(_{0.92}\)Fe\(_{0.08}\)As scan. Error bars, 1 s.d. c, LaOFeAs data again showing both magnetic and nuclear Bragg peaks (data, crosses; Bragg peak positions, short vertical lines) together with the model fit (solid line), at 8 K. Data in a and c were collected using the BT-7 spectrometer with an incident beam wavelength of \(\lambda = 2.44\ \text{Å}\), a PG(0, 0, 2) monochromator and a PG (pyrolytic graphite) filter. Data in b were collected using the HB-1A spectrometer with \(\lambda = 2.36\ \text{Å}\) and a PG filter.
Figure 4 | Temperature dependence of the order parameter at $Q = 1.53\,\text{Å}^{-1}$, obtained using the magnetic structure we determine for LaOFeAs. Blue circles, BT-7 spectrometer data; green squares, HB-1A spectrometer data. The solid line is a simple fit to mean field theory that gives a Neel temperature $T_N = 137(3)$ K. The bottom-left inset shows the temperature dependence of the nuclear $(2, 2, 0)$ peak obtained using the BT-1 diffractometer. It is clear that the lattice is distorted at 138 K, before the long-range static antiferromagnetic order sets in at $-137$ K. The top-right inset shows the antiferromagnetic structure of the system, giving a $2\alpha_\text{N} \times 2\beta_\text{N} \times 2\gamma_\text{N}$ unit cell with moment directions parallel to the planes of iron atoms. To determine the magnetic structure, we note that three magnetic peaks with $h + k + l = 2n$, where $h$, $k$ and $l$ are Miller indices and $n = 0, 1, 2, \ldots$, suggest that the spin configuration has a body-centred symmetry. Our refinements including the spin direction with a $c$-axis component revealed that the $c$ component converged to 0. Because of the very small difference (0.002 Å) in the $a$ and $b$ lattice constants in the orthorhombic magnetic unit cell (see Supplementary Information), it was not possible to determine the spin direction in the $a$–$b$ plane. Error bars, 1 s.d.

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