A Brief Comment on the Low-Temperature Structure of LaOFeAs

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In a recent paper \[\text{arXiv:0804.3569}\], Takatoshi Nomura \textit{et al.} reported a structural phase transition near 150 K in LaOFeAs and used space group "Cmma" to describe their X-ray diffraction data. However, they did not discuss how their proposed structure compares with the early neutron study by Cruz \textit{et al.} [\text{arXiv:0804.0795}] where the low temperature structure of LaOFeAs was described by space group "P112/n". This caused some confusion, suggesting that there may be some disagreement on the low temperature structure of LaOFeAs as evidenced by several inquiries that we received. Here we show that the proposed structures from x-ray and neutron diffraction are basically identical. The P2/c (i.e., P112/n) cell becomes the primitive cell of the Cmma cell when the z-coordinate of the oxygen and iron are assumed to be exactly 0 and 0.5 (these numbers were reported to be -0.0057 and 0.5006 in neutron study). Our first-principles total-energy calculations suggest that the oxygen and iron atoms prefer to lie on the z=0 and 1/2 plane, respectively, supporting Cmma symmetry. However it is more convenient to describe the structural distortion in the primitive P2/c cell which makes it easier to see the connection between the high (i.e., P4/nmm) and low temperature structures.

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The recent discovery of superconductivity at $T_c$'s up to 55 K in layered pnictide-oxide quaternary compounds ROTmPn (R=La, Ce, Sm, Tm=Mn, Fe,Co, Ni, Pn=P, As) has sparked enormous interest in this class of materials\cite{1, 2, 3, 4, 5, 6, 7, 8, 9, 10}. In order to determine the mechanism of superconductivity in these systems, it is very important that we understand the structural properties of the parent compound LaOFeAs first.

To the best of our knowledge, there have been two experimental reports on the low temperature structure of LaOFeAs\cite{7, 8}. The first report\cite{7} is from detailed neutron powder diffraction, which demonstrated that LaOFeAs undergoes an abrupt structural distortion below $\approx 150$ K, changing the symmetry from tetragonal (space group P4/nmm) to monoclinic space group (P112/n or P2/c) at low temperatures. In this neutron study, it was also reported that the system develops long range spin-density wave (SDW) type antiferromagnetic ordering with a small moment and simple stripe like magnetic structure that was first theoretically predicted\cite{6, 9} to occur due to Fermi surface nesting. Our recent computational work\cite{10} based on all-electron density functional theory successfully explains the observed distortion quantitatively as well as the small magnetic moment per Fe. We show that the structural distortion is closely linked to the stripe magnetic ordering which was driven by large antiferromagnetic exchange interaction along the square diagonal of the Fe-lattice and breaks the tetragonal symmetry leading to the observed distortion\cite{10}.

The second experimental report on the low-temperature structure of LaOFeAs comes from Prof. Hideo Hosono’s group\cite{8} [\text{arXiv:0804.3569}]. The authors reported a detailed study based on x-ray powder diffraction. They confirmed the structural phase transition at 150 K in LaOFeAs as observed in the neutron diffraction study of Cruz \textit{et al.}. However the authors described the low-temperature structure by a different space group (Cmma) from the one reported in Cruz \textit{et al.}. Unfortunately they did not compare their proposed Cmma structure with the P2/c structure from neutron data. This caused large confusion in the community as evidenced by many inquiries that we received from different groups. On initial inspection of the x-ray study, one may think that Nomura \textit{et al.} reached a totally different low temperature structure for LaOFeAs than the one reported in the neutron study\cite{7}. However, after a close

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(color online) (Left) The conventional unit cell of LaOFeAs in space group Cmma as described in Ref.[7, 8]. (Right) The primitive cell of the Cmma and its relation to the conventional orthorhombic cell (i.e. $\sqrt{2}\times\sqrt{2}$ cell). The red, light blue, purple, and yellow spheres represent O,La, Fe, and As, respectively.}
\end{figure}
Neutron (4K)

FIG. 2. (color online) The relation between the primitive and the orthorhombic conventional cell in Cmma. The equations relating the orthorhombic lattice parameters, $a_o$ and $b_o$, to the tetragonal-monoclinic distortion (i.e., $\delta$) is given on the right.

Inspection of both reports, one sees that the structures from x-ray and neutron scattering studies are basically identical. In this brief communication, we will compare both structures in detail to show that they are virtually identical.

The Cmma structure proposed in Ref.8 is shown in Fig. 1a. We note that the orthorhombic Cmma structure is the $\sqrt{2} \times \sqrt{2}$ structure discussed in earlier theoretical studies[6, 9, 10]. This is the minimal cell to describe the observed stripe-magnetic ordering. Therefore, when the magnetic ordering is ignored, it is not primitive and actually contains four LaOFeAs unit formula. Fig. 1b shows the primitive cell and its relation to the conventional Cmma cell. From Fig. 1b it is clear that the primitive cell is basically what is proposed in the neutron study[7]. In order to make this point more clear, in Fig 2, we show the relation between the cell parameters of the conventional orthorhombic and primitive monoclinic cells. In particular we emphasize that the tetragonal-orthorhombic distortion described by Nomura et al. is basically the same distortion as described in the neutron study[7], which are essentially no different from 0.5 and 0.0.

In Table I, the structure parameters of LaOFeAs in its low-temperature phase as obtained from x-ray[8] and neutron[7] studies, respectively. The last column gives the differences (in absolute value) between x-ray and neutron structure parameters, which are very small. Note that the x-ray data was taken at 120 K while the neutron data at 4 K. This could be one of the main reasons for the tiny difference between these two structures. The differences in z-values listed in the last column are obtained by using the difference in fractional coordinates from the neutron and the x-ray data times the c-value from the neutron data.

![Diagram](image.png)

FIG. 2: (color online) The relation between the primitive and the conventional monoclinic cells. In particular we emphasize that the primitive cell is basically what is proposed in the neutron study[7]. In order to make this point more clear, in Fig 2, we show the relation between the cell parameters of the conventional orthorhombic and primitive monoclinic cells. In particular we emphasize that the tetragonal-orthorhombic distortion described by Nomura et al. is basically the same distortion as described in the neutron study[7], which are essentially no different from 0.5 and 0.

| X-ray Cmma (120 K) | Neutron (4K) |
|--------------------|--------------|
| Conventional | Primitive | P112/n |
| | | | Diff. |
| a | 5.68262 Å | 4.02806 Å | 4.0275 Å | 0.0006 Å |
| b | 5.71043 Å | 4.02806 Å | 4.0275 Å | 0.0006 Å |
| c | 8.71964 Å | 8.71964 Å | 8.7262 Å | 0.0066 Å |
| $\gamma$ | 90° | 89.7203° | 90.279° |
| $\delta$ | 0.279° | 0.279° | 0.0007° |
| La(z) | 0.14171 | 0.14171 | 0.1426 | 0.0078 Å |
| As(z) | 0.65129 | 0.65129 | 0.6499 | 0.0121 Å |
| O(z) | 0 | 0 | -0.0057 | 0.0497 Å |
| Fe(z) | 0.5 | 0.5 | 0.5006 | 0.0052 Å |

A possible explanation for the tiny difference between the structures listed in Table I is that the x-ray data was taken at $T=120$ K while the neutron data is taken at $T=4$ K. The c-lattice parameter from x-ray and neutron studies seem to be slightly different also. This could be due to oxygen defects that may be present in the samples. At any rate, the structural parameters as well as the z-values of the oxygen and iron ions, which dictates what the symmetry of the final structure will be. Since the numerical difference for these coordinates are very small, this is a technical point rather than quantitative difference in the structures. When the z-values of oxygen and iron are exactly 0 and 0.5, then the symmetry is higher with space group Cmma and the neutron structure becomes the primitive cell of the x-ray structure. These values were reported to be 0.5006 and 0.0057 in the neutron paper[7], which are essentially no different from 0.5 and 0. Hence technically the Cmma and P112/n structures are identical.

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As a final note, we report what the structural optimization from density functional theory gives. As discussed in detail in Ref.[10], both the magnetic and crystal structure are successfully obtained from our calculations. For example, we obtained $a=5.66803$ Å, $b=5.73383$ Å, and $c=8.70417$ Å for the conventional cell, all in excellent agreement with the experimental data. Similarly, the z-values (in fractional coordinates) for the La and As are obtained to be 0.138518 and 0.65155, which are again in
excellent agreement with the data listed in Table 1. Finally, our structural optimization for the z-values of the oxygen and Fe ions always give the high symmetry locations, i.e. 0 and 0.5, respectively, supporting the Cmma symmetry.

In summary, there is no difference in the structure described in x-ray [8] and neutron [7] studies. Technically it seems that Cmma is the correct symmetry where the oxygen and iron ions are at the high symmetry sites (i.e., z=0 and 0.5, respectively). However it is easier to see the connection between the high-temperature tetragonal phase and the low-temperature distorted structure if one works in the primitive cell of Cmma.

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