Ab initio study on structural and electronic properties of ReOFeAs (Re: La, Sm, Nd, Ce, Gd) under hydrostatic pressure

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Abstract
This study employs density-functional theory (DFT) to probe the effect of external pressure on the pristine ReOFeAs (Re: La, Sm, Nd, Ce, Gd). As-Fe-As angle depends non-linearly on pressure. In addition, As-Fe-As angle and As-distance from Fe-layer in SmOFeAs and NdOFeAs obtain a configuration met in unconventional superconductors at around 10 GPa. Last, the structural variations coincide with changes in the electronic density of states which stem from the Re-4f and Fe-3d orbitals.

Introduction
The ‘1111’ iron oxypnictides, ReOFeAs (Re: rear earth) become superconducting (SC) at temperature, Tc, ranging from 26 to 55 K [1]. In ambient conditions, they possess tetragonal structure within P4/nmm space group. They are composed of negatively charged FeAs layers, interlaced by positively charged ReO layers (figure 1) [2].

Spin wave density (SDW) magnetic transition and monoclinic (or orthorhombic) structural phase transition are also common in this family of materials; both emerge at temperature around 150 K, well above Tc [4–6]. Superconductivity in ReOFeAs may arise in response to external pressure or chemical inner pressure - the latter being induced by defects. Several studies reveal that, with the application of external pressure, Tc is enhanced in the underdoped SC compounds and decreased in the overdoped ones, whilst it is not particularly affected in the optimally doped SC compounds [2, 7]. In SC candidates, pressure intercepts structural transition and tends to suppress magnetic ordering [7, 8], although it does not completely eliminate SDW when superconductivity appears [9, 10].

Indicatively, LaOFeAs becomes superconducting with Tc 21 K at 12 GPa [11], defective LaO1-xFxFeAs exhibits Tc, varying from 26 to 43 K at 4 GPa [11], CeO0.7F0.3FeAs is connected with a sharp drop in Tc at 10 GPa [12]. A relatively high Tc, 55 K, has been attained for the defective SmFeAsO1-xFx [13]. It has also been suggested that pristine SmOFeAs exhibits superconductivity under compression higher than 9 GPa [8, 14].

The superconducting phase appears as As height form Fe layer increases up to the threshold 1.38 Ang. and as the As-Fe-As bond angle decreases towards that of regular FeAs4 tetrahedral shape, i.e. 109.47° (figure 1) [15–18]. The distortion in ReO layer is largely involved in the formulation of Fe-As configuration [19]. It has not been experimentally feasible though, to distinguish the lattice effects from that of the carrier doping. Experimentalists have highlighted the need for detailed structural parameters in order to correlate lattice and electronic effects under high pressure [8].

Method
Density functional theory (DFT) periodic calculations were performed, employing the generalized gradient approximation with Perdew-Burke-Ernzerhof (PBE) functionals for the description of exchange and correlation among valence electrons [20]. Pseudopotentials developed according to the Martins Troulier method were
selected to represent the interaction between valence electrons and ionic cores [21]. The van der Waals interactions were accounted by the semi empirical addition of dispersive forces to the PBE functionals with the so called DFT-D method [22]. The DFT + U method was employed to represent on-site Coulomb interactions within the 4 f orbitals of rare earth atoms. A significantly weaker interaction within the 3d orbitals of Fe atoms was assumed. Hubbard potentials, U, of 7 eV and 0.05 eV respectively were selected to avoid errors in the positioning of the electronic states with respect to Fermi level [2, 23, 24]. The plane wave basis set and charge density energy cutoffs were set at 80 Ry and 800 Ry respectively. 20 \times 20 \times 10 Monkhorst Pack k-point grid was found sufficient for the determination of structural parameters. Tetrahedron sampling method [25] was used for the calculation of electronic density of states. The study was implemented in Quantum Espresso (QE) [26].

**Results and discussion**

**Effect on structural parameters**

The unit cell of the ReOFeAs was reproduced setting initial lattice constants a, c at reported experimental values [27–29] and ionic positions at the Wyckoff sites Re 2c ¼ ¼ 0.1, O 2a ¼ ¼ 0, Fe 2b ¼ ¼ ½, As 2c ¼ ¼ 0.6 (figure 1) [28].

Target hydrostatic pressure from 0 to 20 GPa was applied on the unit cell in increments of 2 GPa or less. The cell volume and atomic positions were let to relax towards target pressure in line with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm for force and energy optimization. This procedure was repeated for the relaxed unit cell in order to diminish Pulley stress errors.

The variance of lattice constants, a, c, with pressure is shown in figure 2. Experimentally measured lattice constants are reproduced with less than 1.5% error once employing the DFT-D scheme, as opposed to the plain DFT calculations.

The configuration of the relaxed unit cells at P = 0 GPa was examined for atom—atom contributions to the van der Waals dispersion energy term (E_{disp}) [22].

The major contribution to E_{disp} stems from the interactions between Re atoms at either side of the O layer (table 1). This contribution is one order of magnitude larger than for two C-C atoms in adjacent graphene sheets. Other contributions in the unit cell are comparably negligible.

The space group symmetry was not altered throughout compression; assuming 0.5% initial orthorhombic distortion between a- and b- axes of the SmOFeAs, the unit cell symmetry was restored to tetragonal after relaxation of volume and atomic positions towards 10 GPa.

Figures 3(a), (b) illustrates that, with application of external pressure, As height from Fe layer follows and increasing trend and As–Fe–A angle follows a decreasing trend respectively. LaOFeAs demonstrates an exception to this pattern, fact which is also verified by x-ray diffraction measurements [15].

Noteworthy is the deviation from linearity at around 10 GPa for SmOFeAs, NdOFeAs and CeOFeAs compounds, which is manifested in the curve of lattice constants (figure 2) and crystallographic parameters.
This finding is consistent with diffraction studies in SmOFeAs [29] and NdOFeAsO1−xFy [29]. The defective Ce(O0.84F0.16)FeAs undergoes tetragonal isostructural transition at 13.9 GPa [30]. The variations are featured from the perspective of electronic properties in the following.

Despite the strong covalent nature of Fe-As bond, Fe-As distance drops by 3% from 0 to 40 GPa compression. As pressure escalates, the As atom draws an arc with changing radii around Fe atom on the (010) plane. This distortion is the superposition of compression and pressure-induced torque on the Fe-As bond.

Table 2 lists the values of As-Fe-As angle and As height for Fe layer in ‘1111’ compounds for which superconductivity has been established. The ambient TbFeAsO0.7 so (108.5°/1.38 Ang) [16] and the 15 GPa compressed LaFeAs (114°/1.28) [15, 31] constitute the marginal superconducting configurations.
Figure 3(c) illustrates crystallographic parameters calculated in this study in relation with the superconducting configurations of table 2. It is concluded that, for compression 10 GPa, As-Fe-As angle and As height from Fe layer in SmOFeAs fall well within the range of 1111 superconductors. More particularly, our study yields that As-Fe-As angle changes from 114.9° in the stress-free state to 111.5° and As height from Fe layer rises from 1.2 Ang to 1.3 Ang respectively.
Considering for NdOFeAs that a 2% error in the lattice constants introduces 0.02 Ang error in the calculated As height from Fe layer, NdOFeAs also falls in the superconducting range above 8 GPa, when As-height becomes 1.26–1.27 Ang. and As-Fe-As angle 113.3–113.4°.

According to the same criterion, pristine GdOFeAs and CeOFeAs will not become superconducting regardless of compression; As height form Fe layer in GdOFeAs hardly grows from 1.2 at 0 GPa to 1.214 at 18 GPa. In the pristine CeOFeAs As-Fe-As angle drops from 120° in the stress-free state to 116° above 20 GPa (and becomes 114° close to 40 GPa) whilst As height from Fe layer hardly reaches 1.2 Ang at pressure beyond 20 GPa.

**Effect on electronic and magnetic properties**

Spin polarized calculations were executed on the relaxed unit cells in order to outline magnetic configuration. Among the possible Re-Fe relative magnetic moment orientations—including non magnetic, the antiferromagnetic ordering (figure 1) is energy-favorable.

Total magnetization is formed by contributions from the Re and Fe atoms. In the representative case of SmOFeAs, the magnitude of local magnetization at Sm and Fe atomic sites (interpreted as an estimate of magnetic moment) is 5 μB and 3 μB respectively in the stress-free state. As pressure escalates from 0 to 120 GPa, magnetic moment exhibits a decreasing trend at Sm sites and drops by 7% at Fe sites. However, it is not completely eliminated throughout the compression (figure 4).

In SmOFeAs, the electronic states in the vicinity of Fermi level are populated by electrons occupying primarily Sm 4f orbitals and secondarily Fe 3d orbitals which overlap (figures 5(a), (d)).

The Sm4f orbitals are coupled giving rise to bonding (up) and anti-bonding (down) states near Fermi level at P = 0 GPa. The Fermi level crosses the margin of bonding states, indicating Sm-Sm attraction (figure 5(a)).

In response to external pressure at 10 GPa, the bonding and anti-bonding states are not clearly distinct. Corresponding spin up and spin down states of Sm 4f electrons interfere and lead to a comparably intensified bonding state, favoring Sm-Sm attraction (figure 5(d)).

Fe bonding states interfere with As bonding states 6 eV deeper in the valence band (figures 5(b), (e)). Their density corresponds to strong covalent Fe-As bonds which unambiguously reserve the robustness of crystal structure (figures 5(c), (f)).

| SC compounds               | Tc (K) | External pressure (GPa) | As–Fe–As angle (deg.) | As height from Fe-layer (Ang) | References |
|---------------------------|--------|-------------------------|-----------------------|-------------------------------|------------|
| TbFeAsO0.5                | 53     | 0                       | 108.5                 | 1.38                          | [16]       |
| NdFeAsO0.83               | 50     | 0                       | 110.6                 | 1.37                          | [18]       |
| NdFeAsO0.825              | 35     | 0                       | 111.1                 | 1.35                          | [18]       |
| NdFeAsO0.89–xFx           | 46.3   | 0                       | 111.2                 | 1.36                          | [32]       |
| CeFeAsO0.35              | 40     | 0                       | 112                   | 1.35                          | [16]       |
| PrFeAsO0.80–xFx           | 38.8   | 0                       | 111.95                | 1.34                          | [32]       |
| SmFeAsO0.86–xFx           | 47.9   | 0                       | 110.5                 | 1.36                          | [32]       |
| GdFeAsO0.76–xFx           | 22.7   | 0                       | 109.9                 | 1.37                          | [32]       |
| LaOFeAs                  | 15     | 4.33                    | 114                   | 1.28                          | [15, 31]   |
| LaFeAsO1.27,H0.16 (ambient pressure) | 18 | 0 | 112 | 1.35 | [15] |
| LaFeAsO1.27,H0.16 (7.7 GPa) | 51 | 7.7 | 113 | 1.3  | [15] |

Figure 4. SmOFeAs: Variance of magnetic moment with pressure.

Table 2. Reported As–Fe–As angle and As height from Fe layer for various oxypnictide superconductors.
In CeOFeAs, the presence of Ce (4f) electrons at the Fermi level is weaker than in SmOFeAs (figures 6(a), (d)). Fe-As tetrahedrons not only reserve a robust crystal structure, due to the strong covalent bonds (figures 6(b), (c), (e), (f)), but also inhibit the transition of Fe magnetic ordering to antiferromagnetic at 10 GPa (figures 6(a), (d)). They also provide the Fe (3d) electrons that shift towards and populate Fermi level at 10 Gpa (figure 6(d)).
The Fermi surface for SmOFeAs or CeOFeAs is populated by hole-pockets that grow along the center of Brillouin zone and by electron-pockets around the zone-corners. This pattern is common in '1111' iron oxypnictide superconductors [16]. The electron pockets at the edges of Brillouin zone obtain cylindrical shape, indicating weak dependence on \( k_z \) momentum. External pressure does not have a significant effect on the shape of electron pockets at Brillouin zone edges. On the contrary, the pockets around zone center exhibit stronger
warping dependence on $k_z$ momentum which increases with pressure; in SmOFeAs, the application of 10 GPa pressure results to the hole pocket's near splitting in two lobes (figure 7). The effect of pressure is particularly evident across the $\Gamma$-$\chi$ high symmetry line, where energy bands are segregated so that radii of near-cylindrical Fermi pockets are reduced and the averaged cross section of Fermi surface, $A(E_f)$, is narrowed by half (figures 7(c), (f)). The so reported magnetoresistance oscillations in SmOFeAs [33], with frequency $f = \hbar$c./e $A(E_f)$, will be affected by external pressure.

In CeOFeAs, compression of 10 GPa gives rise to an intrigue pierced Fermi surface with varying curvature (figure 8). Accounting that the crystal structure (As-Fe-As angle, As-height from Fe layer) do not resemble an SC compound, this instability may be connected with the change in magnetic ordering rather than superconductivity.
Conclusions

Van der Waals forces play a significant role in the lattice parameters of ReOFeAs compounds; they are developed primarily between Re atoms and their neighbors and consequently affect atomic positions in the FeAs layer.

These compounds exhibit a complicated behavior under hydrostatic compression. In Sm,Nd, Ce-OFeAs, lattice constants versus pressure deviate from linearity at around $P = 10$ GPa, when As-Fe-As angle may reach a local minimum. These findings are consistent with x-ray diffraction results. However, pressure alone does not alter the tetragonal space group symmetry.

SmOFeAs and NdOFeAs Fe-As tetrahedral obtain configuration similar with that of superconducting compounds above 10 and 8 GPa respectively. CeOFeAs does not obtain such configuration but in undergoes a change in Fe magnetic orientation at 10 GPa.

The structural instabilities at 10 GPa, coincide with changes in the coupling of Re-4f orbitals and Fe-3d orbitals and their overlapping. Spin–orbit interactions between Re-Re and Fe-Fe atoms alter the carrier transfer channels. The modification of the Fermi surface in SmOFeAs drops the frequency of magnetoresistance oscillations by half.

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