

Emergence of Superconductivity in LaOFeAs: Electronic Structure and Lattice Dynamics

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Abstract

In view of continuing interest in the parent compound of the recently discovered superconducting iron-oxypnictide ($\text{LaO}_{1-x}\text{F}_x\text{FeAs}$) we present fresh results and analyses of *ab-initio* calculations of the electronic band structure, lattice dynamical properties, and elastic constants assuming it to be insulating as well as metallic. The total and partial electronic density of states (EDOS) of the undoped LaOFeAs in both states are extracted from the electronic band structure. The phonon dispersion and the phonon density of states (PDOS) are also studied. Possible implications of the band structure, EDOS, and PDOS of LaOFeAs on the eventual appearance of high- T_c superconductivity upon carrier doping are discussed. Our findings reveal that phonons are unlikely to mediate Cooper pairing in RE-OFeAs. In addition, the values of various independent elastic constants of the compound assuming both insulating and metallic states are estimated and discussed.

Keywords: LaOFeAs; Electronic band structure; Phonon spectrum; Elastic constants; Superconductor.

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1. Introduction

Recently a family of rare-earth (RE) iron-oxypnictides (RE-OFeAs) of ZrCuSiAs structure has attracted great deal of interest from the superconductivity researchers. The discovery of superconductivity at $T_c = 26$ K in the fluorine doped $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ [1] and subsequent attainment of a T_c of 55 K in the related $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ compound [2] have generated a flurry of experimental and theoretical activities [3-8]. Like the superconducting cuprates, iron-oxypnictides are quasi two-dimensional (2D), parent materials are antiferromagnetic, and superconductivity occurs upon adding either electrons or holes in the FeAs layers. There is even a pseudogap in the quasiparticle excitation spectrum in these Fe based superconductors [9, 10]. Such similarities with the cuprates have initiated lively debates within the superconductivity community on whether a similar mechanism is at work in both the types [11, 12]. Common to many ideas is that

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Cooper pairing itself may be emergent from more than one competing phases driven by the presence of an underlying quantum critical point.

Understanding the ground state through electronic and lattice dynamical properties of the parent compound is of paramount importance since the emergence of superconductivity on carrier doping or alternatively on suppression of the spin density wave (SDW) [13, 14] must be related to the presence of various interactions in the undoped strongly correlated electronic material. Elastic constants of iron-oxypnictides, on the other hand, are related to the mechanical properties and are of considerable importance in view of future technological applications of these materials. Further knowledge about elastic constants of may provide some ideas about phonon modes. This is because materials having large elastic constants require short and strong chemical bonds and the conditions may indicate the presence of relatively energetic phonon modes. Features of interatomic interactions are related to the electron-ion and electron-electron correlations. It is usually believed that the correlation effects should enhance the effective interaction range, and the manifestations of these effects may be evident in the phonon spectra.

It was found experimentally [15, 16] that the undoped compound shows metallic SDW state with a small ordered magnetic moment at ~ 135 K. The low ordered moment might be due to off-diagonal magnetic frustration in the parent material, as suggested by Rodriguez *et al.* [17]. Since the magnetic moment is highly reduced, a zero spin approximation has some justification, conductivity on the other hand shows ‘bad metallicity’ [18] and its magnitude is rather low for the undoped material. Therefore, several earlier first-principle calculations were done assuming LaOFeAs as an insulator [19-21]. Haule *et al.* [22] computed the electronic structure of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ within the combination of the Density Functional Theory (DFT) and the Dynamical Mean Field Theory (DMFT). They have found that the compound in the normal state is a strongly correlated metal and the parent compound is a bad metal at the verge of a metal insulator transition.

Thus the interest in LaOFeAs has not diminished even after more than a year of the discovery of superconductivity in this type of compound. Very recently Wojdel *et al.* [23] provided strong theoretical evidence showing that, in contrast to previously reported LDA and GGA calculations, LaOFeAs is a complex antiferromagnetic insulator with a physical nature intermediate between Mott-Hubbard and charge-transfer (CT) limiting situations, with important Fe-As covalent interactions and exhibiting a strong spin frustration in its ground state. The conductivity of LaOFeAs samples can be described as typical for thermally activated semiconductors or at most “bad-metals”.

In view of the continuing interest, we are tempted to explore the compound further in this paper. Theoretical calculations are made assuming undoped LaOFeAs as an insulator as well as a metal. We have performed first-principle density functional calculations of the electronic band structure, EDOS, phonon dispersion, PDOS, and the various independent elastic constants for LaOFeAs. We have analyzed the electronic band structure and the phonon spectrum and discussed the possible implications of these on the occurrence of superconductivity in the doped compounds.

2. Method of Computations

The *ab-initio* calculations were performed using the CASTEP program [24]. The geometrical optimization was done for LaOFeAs (space group 129 $P4/nmm$) treating the system as non-spin polarized in both insulating and metallic states. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [25] potentials have been incorporated for the simulation. We have used a $10 \times 10 \times 4$ Monkhorst grid to sample the Brillouin zone. All structures have been fully optimized until internal stress and forces on each atom are negligible. For all relevant calculations the plane wave basis set cut-off used is 380 eV and the convergence criterion is 0.5×10^{-5} eV/atom.

Calculations of phonon spectra, electron-phonon (e-ph) coupling and phonon density of states were performed using plane waves and pseudopotentials with QUANTUM ESPRESSO [26]. We employed ultrasoft Vanderbilt pseudopotentials [27], with a cut-off of 50 Ryd for the wave functions, and 400 Ryd for the charge densities. The k -space integration for the electrons was approximated by a summation over a $8 \times 8 \times 4$ uniform grid in reciprocal space, with a Gaussian smearing of 0.01 Ryd for self-consistent cycles; a much finer ($16 \times 16 \times 8$) grid was used for evaluating the phonon DOS and the e-ph linewidths. Dynamical matrices and e-ph linewidths were calculated on a uniform $4 \times 4 \times 2$ grid in phonon q -space. Phonon dispersions and DOS were then obtained by Fourier interpolation of the dynamical matrices, and the Eliashberg function by summing over individual linewidths and phonons.

3. Results and Discussion

3.1. Geometrical optimization

LaOFeAs has a layered tetragonal crystal structure as shown in Fig. 1. The layers of La-O are sandwiched between layers of Fe-As. The Fe atoms form a square two dimensional lattice with Fe-Fe lattice spacing of 2.85 \AA (assuming a metallic state). The obtained lattice parameters and internal atomic positions of LaOFeAs are given in Table 1 using a

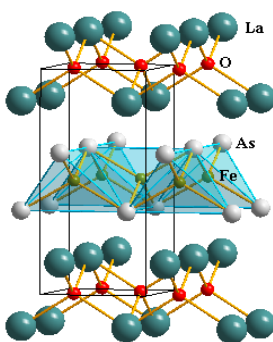


Fig. 1. Tetragonal crystal structure of LaOFeAs compound. FeAs layers are formed by Fe ions tetrahedrally surrounded by As ions.

non-spin polarized calculation. These data are in very good agreement with the experimental results due to Kamihara *et al.* [1] and those determined in Rietveld analysis for undoped LaOFeAs ($P4/nmm$) by Nomura *et al.* [28]. Fe and O atoms sit at the centre of slightly distorted As and La tetrahedra; the As tetrahedra are squeezed in the z direction, so that there are two As-Fe-As angles (θ_1, θ_2), which are either larger or smaller than the regular tetrahedron value ($\theta = 109.47$ deg).

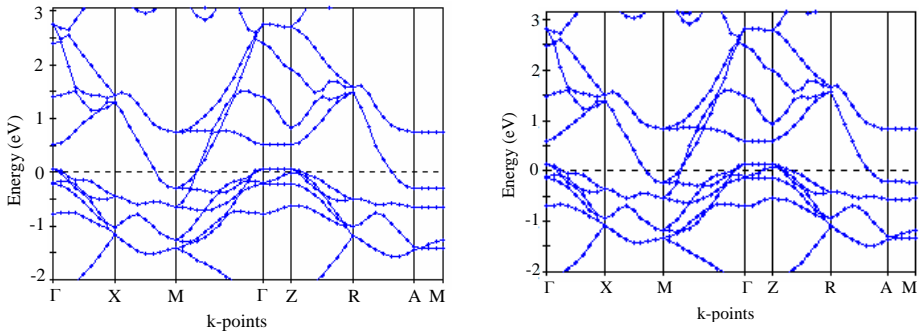
Table 1. Structural parameters of LaOFeAs.

| | a (Å) | c (Å) | V (Å ³) | z_{La} | z_{As} | θ_1 (deg) | θ_2 (deg) |
|---------------|---------|---------|-----------------------|----------|----------|------------------|------------------|
| This (insul.) | 4.0277 | 8.6699 | 140.65 | 0.1490 | 0.6357 | 104.7 | 119.4 |
| This (metal) | 4.0310 | 8.6490 | 140.54 | 0.1489 | 0.6353 | 104.6 | 119.7 |
| Theo. [29] | 3.996 | 8.636 | 137.9* | 0.1413 | 0.6415 | 105.8 | 117.1 |
| Expt. [1] | 4.035 | 8.741 | 142.3* | 0.1415 | 0.6512 | 107.5 | 113.5 |
| Expt. [28] | 4.03268 | 8.7411 | 142.15 | 0.1415 | 0.6512 | | |

*calculated value.

3.2. Electronic band structure and DOS

The material properties can be understood if one can identify the character of dominant bands near the Fermi level, their energy etc. The calculated bands along high symmetry directions of the Brillouin zone and the DOS for pure insulating and metallic states of LaOFeAs are shown in Fig. 2. The bands near the Fermi level distinguish between the two states of the compound.

Fig. 2. Band structure of undoped LaOFeAs assuming insulator (*left*), metal (*right*).

We observe from Fig. 2 that a small dispersion along the c -axis (from Γ to Z and from A to M) which is indicative of weak interactions between LaO and FeAs layers and a 2-dimensional nature of the compound. The bands below E_F are relatively flat and have little

contribution coming from the As-*p* states, while the bands above E_F are quite dispersive, and have large weight coming from the As-*p* character (as discussed below).

The total and the projected density of states of LaOFeAs are shown in Fig. 3 in order to discuss the electronic structure further. It is seen that the dominant states at the Fermi level come mainly from Fe 3*d* atomic states extending roughly between -2.2 eV and 2 eV. This band width of ~ 4.2 eV is ~ 60 % that of metallic bcc Fe, which may suggest significant itinerant character of *d* states [30]. The state energy for O-*p* and As-*p* orbitals are below that for Fe-3*d* and lie within ~ -5.5 eV to -2.2 eV. The Fermi level of the system in the metallic state cuts the band structure in a region where the DOS is 4.0 (2.08, insulating state) states/eV/unit cell. This value is high but decreases rather rapidly. Boeri *et al.* [29] found an energy opening in the electronic spectrum around 0.2 eV. It was indicated in earlier works [4, 22] that such a high DOS near the Fermi level drives the system close to a magnetic instability. On the other hand, the EDOS shows a steep reduction at the Fermi level giving rise to a “bad metallic” behaviour (see Fig. 3). The EDOS at the Fermi level is higher when a metallic picture is invoked.

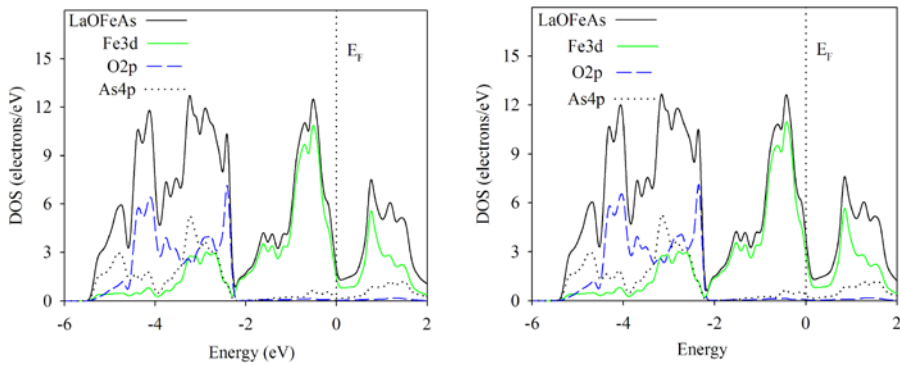


Fig. 3. Density of states (DOS) of undoped LaOFeAs as insulator (left), metal (right).

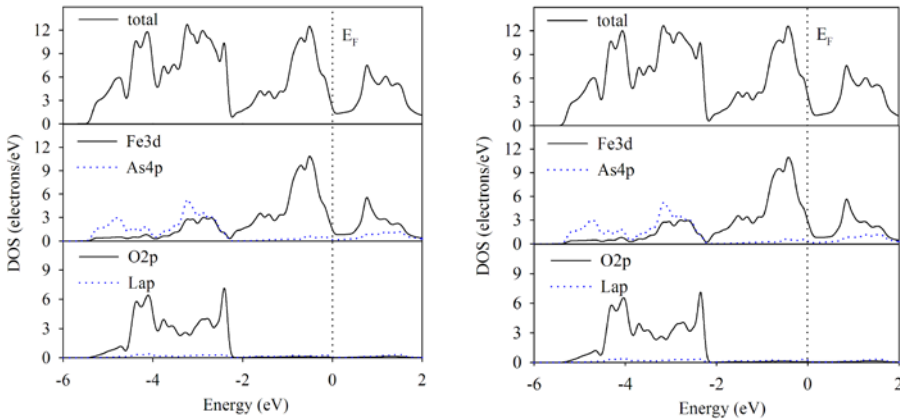


Fig. 4. Total (upper panel) and partial densities of states for LaOFeAs as insulator (left), metal (right).

We note that electronic states of La-O layers are rather far from the Fermi level. Nekrasov *et al.* [31] have also shown that the electronic structure of RE-OFeAs compounds (e.g. the DOS around the Fermi level) practically does not depend on the kind of rare-earth ion used in a wide energy interval around the Fermi level, which is relevant for superconductivity in FeAs layers. Thus the p - d hybridization between O and Fe (as illustrated by partial DOS contributions shown in Fig. 4) is negligible. But within the FeAs layers a quite sizeable mixing between Fe- d and As- p is apparent around -3.2 eV (nearly same for metallic state also) where As 4 p band is strongly peaked (see Fig. 4). Therefore, LaOFeAs can be considered as a quasi-2D which looks to be similar to the case of conventional high- T_c cuprates.

It may be pointed out here that the simple tetrahedral crystal field predicts that the five d orbitals split into low-lying two-folds e_g states and up-lying three-folds t_{2g} states. The distortion of the tetrahedron from its normal shape (see Table 1) will further split the e_g and t_{2g} manifolds significantly making the final orbital distributions complicated [29, 32]. The manifold is two-folds, between which an energy gap of about 0.5 eV exists. The nominal number of d electrons in LaOFeAs is 6, and the low-lying three-fold bands are nearly fully occupied with the Fermi level, E_F , located close to the energy gap, and therefore the non-magnetic ground state is stabilized [32].

3.3. Phonon spectrum and electron-phonon coupling

Fig. 5 shows the calculated phonon dispersions of LaOFeAs in the metallic state and the corresponding phonon density of states (on the right panel of the figure). The phonon dispersions show a set of 24 phonon branches since there are two formula units per primitive cell. The spectrum extends up to 500 cm^{-1} ; it shows three main peaks centred at $\sim 105 \text{ cm}^{-1}$ and smaller peaks at $\sim 180 \text{ cm}^{-1}$ and $\sim 265 \text{ cm}^{-1}$.

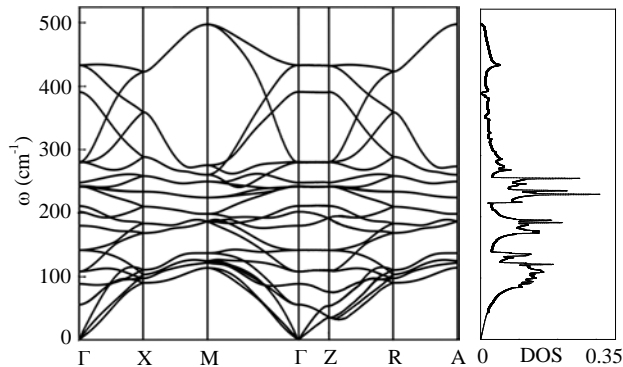


Fig. 5. Electron-phonon properties of LaOFeAs. *Left*: Phonon dispersion relations; *Right*: Phonon DOS.

Similar observations were reported earlier by other workers [4, 29]. The higher frequency manifold is due mainly from vibrations of O atoms which are dispersive and well separated in energy from those other atomic species [29]. The lower manifold from 0 to 200 cm^{-1} consists of the acoustic modes and modes of mixed, but mainly metal character. Further the projection on in- and out-of-plane modes (not shown) does not show any clear separation between the patterns of vibration. This is contrary to what is expected in a layered compound like LaOFeAs. Thus the three major peaks cannot be attributed to a single vibration pattern [29]. Our calculated phonon spectra agree quite well with earlier calculations based on non-spin polarized model and experimental results [29].

The frequency-dependent e-ph coupling constant $\lambda(\omega)$ and Eliashberg function $\alpha^2F(\omega)$ are given by [33]

$$\lambda(\omega) = 2 \int_0^\omega d\Omega \alpha^2 F(\Omega) / \Omega \quad (1)$$

$$\alpha^2 F(\omega) = \frac{1}{N(0)} \sum_{nmk} \delta(\varepsilon_{nk}) \delta(\varepsilon_{mk+q}) \sum_{vq} |g_{v,nk,m(k+q)}|^2 \delta(\omega - \omega_{vq}) \quad (2)$$

where $g_{v,nk,mk}$ are the bare DFT matrix elements.

The total e-ph coupling constant λ for metallic state of LaOAsFe, is obtained by numerical integration of Eq. (1) up to $\omega = \infty$ and is shown Table 2.

Table 2. Electron-phonon properties.

| Ref. | $N(0)$ $\text{eV}^{-1}\text{f.u}^{-1}$ | ω_{in} (K) | λ | μ^* | T_c (K) |
|------|---|-----------------------------|-----------|-----------|--------------|
| This | 2.16 | 221 | 0.13 | 0 0.12 | 0.12 0 |
| [28] | 2.1 | 205 | 0.21 | 0 | 0.5 |

The resulting value of λ is almost the same as that obtained earlier by Boeri *et al.* [29] and Mazin *et al.* [34]. The logarithmically-averaged frequency ω_{in} , is calculated to be 221 K. We use $\mu^* = 0$ and 0.12 in the simplified Allen-Dynes formula for T_c [35]:

$$k_B T_c = \frac{\hbar\omega_{\text{in}}}{1.2} \exp \left[- \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \quad (3)$$

This gives $T_c = 0.12$ K for $\mu^* = 0$ (Table 2) which is too small to explain the $T_c = 26$ K observed in doped sample. Boeri *et al.* [29] noted that the undoped LaOFeAs is close to a magnetic instability, due to the presence of a very sharp peak in the electronic density of states. The system moves away from the magnetic instability on doping with electrons. This causes the reduction of the DOS near the Fermi level, without changing the band

structure appreciably and without introducing new bands at E_F . Thus the net result of such doping would be to reduce the value of λ . Therefore, the value $\lambda = 0.13$ for the undoped material is actually an upper bound for the value in the e-doped compound. This value is lower than what is seen in any known e-ph superconductor, e.g., $\lambda = 0.44$ in metallic aluminium ($T_c = 1.3$ K).

3.4. Elastic constants

Table 3 shows the calculated six independent elastic constants, C_{ij} for the tetragonal LaOFeAs along with the results obtained by Shein and Ivanovskii [19]. The elastic constants are all positive and satisfy the well-known Born's criteria for tetragonal crystals: $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$ and $[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0$. All these imply the mechanical stability of the crystal.

Table 3. Calculated elastic constants, C_{ij} for monocrystalline LaOFeAs phase. Bulk and shear moduli (B_V , G_V) are for macroscopic material in the Voigt approximation.

| C_{ij} (GPa) | LaOFeAs | | |
|-------------------|-----------|-------|-----------|
| | This work | | [19] |
| | Insulator | Metal | Insulator |
| C_{11} | 218.5 | 213.6 | 191.9 |
| C_{12} | 75.5 | 80.4 | 55.9 |
| C_{13} | 87.8 | 93.7 | 61.6 |
| C_{33} | 151.0 | 138.2 | 144.8 |
| C_{44} | 63.8 | 61.9 | 44.1 |
| C_{66} | 68.0 | 69.0 | 77.9 |
| B_V | 121.1 | 122.3 | 98.5 |
| G_V | 61.6 | 58.4 | 56.5 |

LaFeAsO is usually prepared and investigated as polycrystalline ceramics in the form of aggregated mixtures of micro-crystallites with a random orientation. Thus it is quite useful to estimate the corresponding parameters for these polycrystalline materials. The theoretical polycrystalline elastic moduli for LaOFeAs may be calculated from the set of six independent elastic constants. Hill [36] proved that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants. He showed that the polycrystalline moduli are the arithmetic mean values of the moduli in the Voigt (B_R , G_R) and Reuss (B_R , V_R) approximation, and are thus given by $B_H \equiv B = \frac{1}{2}(B_R + B_V)$ and $G_H \equiv G = \frac{1}{2}(G_R + G_V)$. The expression for Reuss and Voigt moduli can be found elsewhere [37, 38]. From the calculated values of the moduli it is easy to evaluate the compressibility (β), Young's moduly (Y), and the Poisson's ratio (ν) (see Table 4).

Table 4. Calculated elastic parameters for polycrystalline LaOFeAs.

| | B (GPa) | β (GPa ⁻¹) | G (GPa) | Y (GPa) | ν |
|------------------|-----------|------------------------------|-----------|-----------|-------|
| Insulator (This) | 119.7 | 0.00835 | 60.2 | 154.7 | 0.285 |
| Metal (This) | 120.2 | 0.00832 | 55.9 | 145.2 | 0.298 |
| Insulator [19] | 97.9 | 0.01022 | 56.2 | 141.5 | 0.259 |

The results obtained are presented in Table 3 from which we see that $B_V > G_V$. The shear modulus G_V is parameter which limits the mechanical stability of a material. This is apparent due to the layered structure of the compound.

As compared with other superconductors, LaOFeAs is a soft material. This is evident from the value of relatively smaller bulk moduli for LaOFeAs (~120 GPa), which is smaller than the bulk moduli of other well known superconducting materials such as MgB₂, MgCNi₃, YBCO and YNi₂B₂C [39-42].

Finally, the criterion of brittleness of a material is $B/G < 1.75$ [43]. According to this LaOFeAs lies just above the border of brittleness as B/G is 2.15 (metal) and 1.99 (insulator). These values can be compared with 1.74 (insulator) obtained by Shein and Ivanovskii [19]. It is known that the values of the Poisson Ratio (ν), minimal for covalent materials ($\nu = 0.1$), increase for ionic systems [44]. In our case, the value of ν for LaOFeAs assuming metal is 0.298, which is indicative of sizable ionic contribution in intra-atomic bonding.

4. Conclusion

The lattice parameters and internal atomic coordinates of LaOFeAs using non-spin polarized calculation are in very good agreement with the experimental results. The electronic band structure reveals that the dominant states at the Fermi level come mainly from Fe 3*d* atomic states extending roughly between -2.2 eV and 2 eV. The Fermi level is located at the shoulder just below the dip in the *d* band. We find a high density of states which decreases very rapidly. Such a high DOS close to the Fermi level drives the system close to a magnetic instability. The low DOS at the Fermi level gives rise to the bad-metallic behaviour. The calculated elastic constants and the phonon spectra are rather insensitive to the assumptions whether the ground state is insulating or metallic.

The electronic states of La-O layers are rather far from the Fermi level. The *p-d* hybridization between the lighter most O and Fe is negligible. But within the FeAs layers a quite sizeable mixing between Fe-*d* and As-*p* is apparent around -3.2 eV where As 4*p* band is strongly peaked. The strongly delocalized character of the Fe-*d* states at ± 2 eV around the Fermi level is responsible for very small e-ph matrix elements yielding a small λ . We see that such behaviour is an intrinsic property of this LaOFeAs, which is unlikely to be changed by external parameters, such as pressure or doping [29]. To explain the observed T_c in the system one would need further mechanism beyond the conventional e-

ph theory. The mixed nature of the phonon spectrum indicates that conventional elemental isotope substitution experiments will not be able to identify the role played by specific phonon modes in superconducting pairing, if any. Due to the magnetic instability observed in the parent material, spin fluctuations may lead to Cooper pairing in the RE-OFeAs compounds. Indeed, a popular suggestion have been one that assigns the role of the mediating boson to spin fluctuations with wave vectors close to $\mathbf{Q} = (\pi, \pi)$ [45].

The analysis of elastic constants shows that LaOFeAs is a mechanically stable anisotropic material. The phase is a soft material (high compressibility) and lies just above the borderline of brittleness. Sizable ionic contribution in intra-atomic bonding in the compound is also predicted.

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References

1. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008). [doi:10.1021/ja800073m](https://doi.org/10.1021/ja800073m)
2. J. Yang, Z. -C. Li, W. Lu, W. Yi, X. -L. Shen, Z.-A. Ren, G. -C. Che, X.-L. Dong, L. -L. Sun, and F. Zhou, *Supercond. Sci. Technol.* **21**, 082001 (2008). [doi:10.1088/0953-2048/21/8/082001](https://doi.org/10.1088/0953-2048/21/8/082001)
3. A. B. Vorontsov, M. G. Vavilov, and A. V. Chubukov, *Phys. Rev. B* **79**, 060508 (2009). [doi:10.1103/PhysRevB.79.060508](https://doi.org/10.1103/PhysRevB.79.060508)
4. D. J. Singh and M. -H. Du, *Phys. Rev. Lett.* **100**, 237003 (2008). [doi:10.1103/PhysRevLett.100.237003](https://doi.org/10.1103/PhysRevLett.100.237003)
5. L. S. Mazov, arXiv: 0805.4097.
6. A. V. Chubukov, D. Efremov, and I. Eremin, *Phys. Rev. B* **78**, 134512 (2008). [doi:10.1103/PhysRevB.78.134512](https://doi.org/10.1103/PhysRevB.78.134512)
7. M. D. Johannes and I. I. Mazin, *Phys. Rev. B* **79**, 220510 (2009). [doi:10.1103/PhysRevB.79.220510](https://doi.org/10.1103/PhysRevB.79.220510)
8. P. V. Sushko, A. L. Schluger, M. Hirano, and H. Hosono, *Phys. Rev. B* **78**, 172508 (2008). [doi:10.1103/PhysRevB.78.172508](https://doi.org/10.1103/PhysRevB.78.172508)
9. Y. Ishida, T. Shimojima, K. Ishizaka, T. Kiss, M. Okawa, T. Togashi, S. Watanabe, X.-Y. Wang, C.-T. Chen, Y. Kamihara, M. Hirano, H. Hosono, and S. Shin, arXiv: 0805.2647v1.
10. K. Ishida, Y. Nakai, and H. Hosono, *J. Phys. Soc. Jpn.* **78**, 062001 (2009). [doi:10.1143/JPSJ.78.062001](https://doi.org/10.1143/JPSJ.78.062001)
11. I. I. Mazin and M. D. Johannes, *Nature Physics* **5**, 141 (2009). [doi:10.1038/nphys1160](https://doi.org/10.1038/nphys1160)
12. E. Berg, S. A. Kivelson, and D. J. Scalapino, *New Journal of Physics* **11**, 085007 (2009). [doi:10.1088/1367-2630/11/8/085007](https://doi.org/10.1088/1367-2630/11/8/085007)
13. Z. Zhong, Q. Zhang, P. X. Xu, and P. J. Kelly, arXiv: 0810.3246v1.
14. D. J. Singh, arXiv: 0901.2149v1.
15. R. H. Liu, G. Wu, T. Wu, D. F. Fang, H. Chen, S. Y. Li, K. Liu, Y. L. Xie, X. F. Wang, R. L. Yang, L. Ding, C. He, D. L. Feng, and X. H. Chen, *Phys. Rev. Lett.* **101**, 087001 (2008). [doi:10.1103/PhysRevLett.101.087001](https://doi.org/10.1103/PhysRevLett.101.087001)
16. T. M. McQueen, M. Regulacio, A. J. Williams, Q. Huang, J. W. Lynn, Y. S. Hor, D. V. West, M. A. Green, and R. J. Cava, *Phys. Rev. B* **78**, 024521 (2008). [doi:10.1103/PhysRevB.78.024521](https://doi.org/10.1103/PhysRevB.78.024521)

17. J. P. Rodriguez and E. H. Rezayi, *Phys. Rev. Lett.* **103**, 097204 (2009).
[doi:10.1103/PhysRevLett.103.097204](https://doi.org/10.1103/PhysRevLett.103.097204)
18. C. Wang, S. Jiang, Q. Tao, Z. Ren, Y. Li, L. Li, C. Feng, J. Dai, G. Cao and Z. Xu, arXiv: 0811.3925v1.
19. I. R. Shein and A. L. Ivanovskii, arXiv: 0807.3422.
20. I. Shein, A. Ivanovskii, *Scripta Materialia* **59**, 1099 (2008).[doi:10.1016/j.scriptamat.2008.07.028](https://doi.org/10.1016/j.scriptamat.2008.07.028)
21. I. R. Shein and A. L. Ivanovskii, arXiv: 0807.0984.
22. K. Haule, J. H. Shim, and G. Kotliar, *Phys. Rev. Lett.* **100**, 226402 (2008).
[doi:10.1103/PhysRevLett.100.226402](https://doi.org/10.1103/PhysRevLett.100.226402)
23. J. C. Wojdeł, I. P. R. Moreira, and F. Illas, *J. Am. Chem. Soc.* **131**, 906 (2009).
[doi:10.1021/ja808519y](https://doi.org/10.1021/ja808519y)
24. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, and M. C. Payne, *Zeitschrift fuer Kristallographie* **220**, 567 (2005). [doi:10.1524/zkri.220.5.567.65075](https://doi.org/10.1524/zkri.220.5.567.65075)
25. J. P. Perdew, S. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
[doi:10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865)
26. P. Giannozzi, S. Baroni, N. Bonin, M. Calandra, R. Car, C. Cavazzoni, Ceresoli, D. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens.Matter* **21** 395502(2009). <http://www.quantum-espresso.org>; [doi:10.1088/0953-8984/21/39/395502](https://doi.org/10.1088/0953-8984/21/39/395502)
27. D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990). [doi:10.1103/PhysRevB.41.7892](https://doi.org/10.1103/PhysRevB.41.7892)
28. T. Nomura, S. W. Kim, Y. Kamihara, M. Hirano, P. V. Sushko, K. Kato, M. Takata, A. L. Shluger, and H. Hosono, cond-mat/arXiv:0804.3569; and also *J. Phys. Soc. Jpn. Suppl. C*, **77**, 32 (2008). [doi:10.1143/JPSJ.77.024701](https://doi.org/10.1143/JPSJ.77.024701)
29. L. Boeri, O. V. Dolgov, and A. A. Golubov, *Phys. Rev. Lett.* **101**, 026403 (2008).
[doi:10.1103/PhysRevLett.101.026403](https://doi.org/10.1103/PhysRevLett.101.026403)
30. S. Ishibashi, K. Terakura, and H. Hosono, *J. Phys. Soc. Jpn.* **77**, 053709 (2008).
[doi:10.1143/JPSJ.77.053709](https://doi.org/10.1143/JPSJ.77.053709)
31. I. A. Nekrasov, Z. V. Pchelkina, M. V. Sadovskii, *Pis'ma v ZhETF.* **87**, 647 (2008).
32. G. Xu, W. Ming, Y. Yao, X. Dai, S. Zhang, and Z. Fang, *Europhysics Letters* **82**, 67002 (2008).
[doi:10.1209/0295-5075/82/67002](https://doi.org/10.1209/0295-5075/82/67002)
33. G. M. Eliashberg, *Sov. Phys. JETP* **11**, 696 (1960) and G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.* **38**, 966 (1960).
34. I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, *Phys. Rev. Lett.* **101**, 057003 (2008).
[doi:10.1103/PhysRevLett.101.057003](https://doi.org/10.1103/PhysRevLett.101.057003)
35. P. B. Allen and R. C. Dynes, *Phys. Rev. B* **12**, 905 (1975). [doi:10.1103/PhysRevB.12.905](https://doi.org/10.1103/PhysRevB.12.905)
36. R. Hill, *Proc. Phys. Soc. London A* **65**, 349 (1952). [doi:10.1088/0370-1298/65/5/307](https://doi.org/10.1088/0370-1298/65/5/307)
37. A. Reuss, *Z. Angew. Math. Mech.* **9**, 49 (1929). [doi:10.1002/zamm.19290090104](https://doi.org/10.1002/zamm.19290090104)
38. W. Voigt. *Lehrbuch der Kristallphysik*, Teubner, Leipzig. (1928).
39. S. Meenakshi, V. Vijayakumar, R. S. Rao, B.K. Godwal, S. K. Sikka, P. Ravindran, Z. Hossain, R. Nagarajan, L. C. Gupta, R. Vijayaraghavan, *Phys. Rev. B* **58**, 3377 (1998).
[doi:10.1103/PhysRevB.58.3377](https://doi.org/10.1103/PhysRevB.58.3377)
40. U. Jaenicke-Rossler, G. Zahn, P. Paufler, B. Wehner, H. Bitterlich, *Physica C* **305**, 209 (1998).
[doi:10.1016/S0921-4534\(98\)00327-X](https://doi.org/10.1016/S0921-4534(98)00327-X)
41. H. Y. Wang, X. R. Chen, W. J. Zhu, Y. Cheng, *Phys. Rev. B* **72**, 172502 (2005).
[doi:10.1103/PhysRevB.72.172502](https://doi.org/10.1103/PhysRevB.72.172502)
42. I. R. Shein, V. V. Bannikov, A. L. Ivanovskii, *Physica C* **468**, 1 (2008).
[doi:10.1016/j.physc.2007.08.004](https://doi.org/10.1016/j.physc.2007.08.004)
43. S. F. Pugh, *Phil. Mag.* **45**, 833 (1954).
44. J. Haines, J. M. Leger, G. Bocquillon, *Ann. Rev. Mater. Res.* **31**, 1 (2001).
[doi:10.1146/annurev.matsci.31.1.1](https://doi.org/10.1146/annurev.matsci.31.1.1)
45. I. I. Mazin, arXiv:0909.5174v1.