Is LaO$_{1-x}$F$_x$FeAs an electron-phonon superconductor?

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The very recent report of superconductivity with the remarkable $T_c$ of 26 K in LaO$_{1-x}$F$_x$FeAs [1] has stimulated an intense experimental and theoretical activity, aimed at identifying the possible superconducting mechanism. This compound belongs to a family of quaternary oxypnictides of the form LnOMPn, where Ln=La and Pr, M=Mn, Fe, Co and Ni; Pn=P and As, synthesized in 1995. [2] Superconductivity was first reported in LaOF$_x$P, with a relatively low $T_c$ of $\sim$ 7 K [3], and later in F-doped LaOF$_x$As, with a maximum $T_c$ of 26 K at $x$=0.12 (apparently pure LaOF$_x$As shows no superconductivity).

The first bulk measurements on a sample with $x$ = 0.1 have shown that F-doped LaOF$_x$As has a relatively small in-plane coherence length ($\xi_{ab} = 81\AA$) and a $T$-dependent Hall coefficient [4], the electronic specific heat displays a vanishingly small jump at $T_c$, and its behavior under magnetic field [5] as well as point-contact spectroscopy [6] suggest the presence of nodes in the superconducting gap. All these observation suggest a strong analogy with the high-$T_c$ cuprates.

A recent LSDA calculation predicts that pure LaOF$_x$As is on the verge of a ferromagnetic instability, due to a very high Density of States (DOS) of Fe $d$ electrons at the Fermi level. [7] A DMFT calculation in the paramagnetic phase, including strong-correlation effects beyond LDA, shows that for $U$ = 4 eV, a large amount of spectral weight is shifted away from the Fermi level, and the undoped system has a bad metallic behaviour. [8] Both papers rule out standard $e- ph$ theory as a possible explanation for superconductivity, without estimating the magnitude of the $e- ph$ coupling constant.

In this Letter, we calculate from first-principles the electron-phonon properties of LaOF$_x$As, using Density Functional Perturbation Theory [10, 11]. Similar calculations, in conjunction with Migdal-Eliashberg theory, reproduced the superconducting properties of many standard $e- ph$ superconductors [11], including MgB$_2$ [12] with considerable accuracy. On the other hand, they fail dramatically in the the High-$T_c$ cuprates, [13, 14] where the Local Density Approximation is not sufficient to describe the strong local electronic correlations, and their interaction with phonons. [15]

Our calculations show that LaOF$_x$As is intrinsically a very poor $e- ph$ superconductor, with a very weak $e- ph$ coupling distributed evenly over several phonon branches. For electron-doped LaOF$_x$As we calculate an upper limit for the $e- ph$ coupling constant $\lambda \sim 0.21$, which, together with $\omega_{\text{fn}} = 206K$, is a factor 5 too small to account for the observed $T_c = 26K$.

LaOF$_x$As crystallizes in a tetragonal crystal structure (space group 129), with $a = 4.035(3.996)\AA$, $c = 8.741(8.636)\AA$; [16] La and As atoms occupy 2c Wyckoff positions, with $z = 0.145(0.143)$ and $z = 0.6512(0.6415)$ respectively; O and Fe atoms occupy 2a and 2b Wyckoff positions.

The structure, depicted in Fig. 1, consists of alternating Fe-As and La-O layers. Fe and O atoms sit at the

FIG. 1: (color online) Crystal structure of LaOF$_x$As.
center of slightly distorted As and La tetrahedra; the As tetrahedra are squeezed in the z direction; the Fe-As distance is 2.41 (2.34) Å, and the As-Fe-As angles are either 107.5 (105.8) or 113.5 (117.1) degrees. Fe atoms also bond to other Fe atoms in plane, which are arranged on a square lattice at a distance of 2.85 (2.83) Å.

The gross features of the band structure of LaOFeAs are very similar to those of LaOFEP. Measuring energies from the Fermi level, O p and As p states form a group of 12 bands extending from ∼ −6 to −2 eV. La-f states are found at higher energies, at ∼ 2 eV. Apart from a weak hybridization of the $t_{2g}$ states with$cations such a high DOS at the Fermi level drives the system close to a magnetic instability.

The Fermi surface comprises a doubly-degenerate cylindrical hole pocket centered at the Γ point, and a doubly-degenerate electron pocket centered at the M point; these sheets have a dominant $d_{xz}$, $d_{yz}$ character. A small 3D pocket centered around the Γ point is also present (see Fig. 3 of Ref. [8]). The plasma frequencies are strongly anisotropic ($\omega_{xx} = 3.30, \omega_{zz} = 0.32$ eV). The distortion (elongation or shrinking) of the Fe-As tetrahedra modulates the splitting of the two $d_{3z^2-1}$ bands, and the relative splitting between $xy$ and $xz, yz$ bands along the Γ-Z line, as indicated by the small arrows Fig. As tetrahedra are squeezed in the Knudsen structure around 0° decreasing; a pseudo-gap opens in the electronic spectrum around ±0.5 eV.

As p states, at −3 eV, the ten Fe−d states are localized in an energy window extending ±2 eV around the Fermi level, where they give the dominant contribution to the DOS. The derived bands do not split simply into a lower $e_g$ ($d_{x^2−y^2}$ and $d_{3z^2−1}$) and higher $t_{2g}$ manifold, as predicted by crystal field theory (see Fig. 2). Due to the presence of Fe-Fe directed bonds, $d_{x^2−y^2}$ orbitals, which lie along the bonds, create a pair of bonding-antibonding bands located at −2 and +1 eV. $d_{3z^2−1}$ bands states split into two sub-bands. Due to the distortion of the Fe-As tetrahedra, $d_{xy}$ states are inequivalent to $d_{xz}, d_{yz}$ states, and the resulting the $t_{2g}$ bands form a complicated structure centered at ∼ −0.5 eV.

The Fermi level cuts the band structure in a region where the DOS is high (2.1 states/eV spin) and rapidly decreasing; a pseudo-gap opens in the electronic spectrum around 0.2 eV. As pointed out in previous publi-
tern. This complicates the interpretation of the Eliashberg spectral function \( \alpha^2 F(\omega) \), shown in the rightmost panel of Fig. 3 together with the frequency-dependent \( e - ph \) coupling constant \( \lambda(\omega) \):

\[
\alpha^2 F(\omega) = \frac{1}{N(0)} \sum_{m,n,k} \delta(\epsilon_{mn}) \delta(\epsilon_{mk+q}) \times \\
\times \sum_{\nu q} |g_{\nu, m, n, k+q}|^2 \delta(\omega - \omega_{\nu q}); \quad (1)
\]

\[
\lambda(\omega) = 2 \int_0^\infty d\Omega \frac{\alpha^2 F(\Omega)}{\Omega} \quad (2)
\]

A comparison of the Eliashberg function with the phonon DOS shows that, except for the high-lying O modes, which show very little coupling to electrons, the \( e - ph \) coupling is evenly distributed among all the phonon branches. Low-frequency phonons around 100 cm\(^{-1}\) provide \( \sim 75\% \) of the total \( \lambda \), due to the 1/\( \Omega \) factor in Eq. (2) but the \( e - ph \) matrix elements \( g \) are comparable for all group of phonons.

It is interesting to note that this almost perfect proportionality between the Eliashberg function and the phonon DOS is never encountered in good \( e - ph \) superconductors, where the coupling to electrons is usually concentrated in a few selected phonon modes. This is best explained in terms of phonon patterns that awake dormant \( e - ph \) interaction between strongly directed orbitals.

An extreme example in this sense is MgB\(_2\), which achieves a \( T_c \) of 39 K thanks to a strong coupling between bond-stretching phonons and strongly covalent \( \sigma \) bands, but the same applies also to more traditional superconductors, such as the A15, NbC, and even normal metals.

In LaOFe\(_2\)As, all phonon modes give a comparable, small contribution to the total \( \lambda \); this indicates that there are no patterns of vibration with a dramatic effect on the electronic band structure around the Fermi level. A posteriori, this is not surprising since in LaOFe\(_2\)As the only bands derived from directed bonds, (\( d_{z^2 - r^2}\) in Fig. 1), which could experience strong coupling to Fe vibrations in plane, sit far from the Fermi level.

The distribution of the coupling is also shown in the left panel of Fig. 3 where the radius of the circles is proportional to the mode \( \lambda \), i.e. to the partial contribution of each phonon mode to the total e-ph coupling

\[
\lambda(\omega) \equiv \frac{1}{\pi N(0)} \frac{\gamma_{\nu q}}{\omega_{\nu q}^2}, \quad (3)
\]

where \( \gamma_{\nu q} \) are the e-ph linewidths; summing Eq. (3) over the phonon branches \( \nu \) and averaging on the BZ gives the total e-ph coupling \( \lambda \). The circles are evenly distributed over several phonon branches. The largest couplings are concentrated around the \( \Gamma(Z) \) points, where the intraband nesting is large, and around the \( M \) point, where the interband nesting between the hole and electron cylinders take place.

The total \( e - ph \) coupling constant \( \lambda \), obtained by numerical integration of Eq. (2) up to \( \omega = \infty \), is 0.21; this, together with a logarithmically-averaged frequency \( \omega_{\nu a} = 205 K \), and \( \mu^* = 0 \), gives \( T_c = 0.5 K \) as an upper bound for \( T_c \), using the Allen-Dynes formula [17]. Numerical solution of the Eliashberg equations with the calculated \( \alpha^2 F(\omega) \) function gives \( T_c = 0.8 K \). To reproduce the experimental \( T_c = 26 K \), a five times larger \( \lambda \) would be needed, even for \( \mu^* = 0 \). Such a large disagreement clearly indicates that standard \( e - ph \) theory cannot be applied in LaOFe\(_2\)As, in line with recent theoretical works which emphasize the role of strong electronic correlations and/or spin fluctuations [8, 9].

The numerical uncertainty on the calculated value of \( \lambda \), connected to limited sampling of the BZ in \( k \) (electrons) or \( q \) (phonons) space integration, is at most 0.1, and definitely not sufficient to raise \( \lambda \) to \( \sim 1.0 \). We further notice that electron doping, reducing the DOS at the Fermi level, without introducing new bands at \( E_F \), would further reduce the value of \( \lambda \). Therefore, the value \( \lambda = 0.21 \) for the undoped material is actually an upper bound for the value in the e-doped compound. This value is lower than what is encountered in any known \( e - ph \) superconductor; for comparison, \( \lambda = 0.44 \) in metallic aluminum, where \( T_c = 1.3 K \).

In LaOFe\(_2\)As, both the electronic DOS at the Fermi level, and the value of the average phonon force constant are in line with those of other \( e - ph \) superconductors. The occurrence of a small \( \lambda \) is due to its extremely small
matrix $e-ph$ elements, connected to the strongly delocalized character of the Fe-d states at $\pm 2$ eV around the Fermi level. This is an intrinsic property of this material, which could hardly be modified by external parameters, such as pressure or doping. For the same reason, our result is quite stable with respect to the minor differences in the electronic structure around the Fermi level, which have been observed in literature.

In principle, multiband and/or anisotropic coupling could provide the missing factor 5 in the coupling, but this is very unlikely to occur because it would require a very large anisotropy of the distribution. Other interactions, repulsive in the s-wave channel but attractive in the d- or p-wave one, may increase $T_c$.

In conclusion, we have calculated the electron-phonon properties of the newly discovered superconductor $\text{La[O}_{1-x}\text{F}_x\text{]}\text{FeAs}$ using Density Functional Perturbation Theory. The undoped compound is close to a magnetic instability, due to the presence of a very sharp peak in the electronic Density of States. Doping with electrons moves the system away from the magnetic instability, reducing the DOS at the Fermi level, without altering the band structure substantially.

Despite the high value of the DOS at the Fermi level, the calculated value of the e-ph coupling constant for the pure compound is only $\lambda = 0.21$, which is a factor 5 too small to yield the experimentally measured $T_c$ within the scope of standard ME theory.

The value $\lambda = 0.21$ in LaOFeAs is very close to those which have been estimated using LDA in the superconducting cuprates ($\lambda \sim 0.3$). Similarly to the superconducting cuprates, in this compound superconductivity cannot be described using standard LDA calculations and Migdal-Eliashberg theory. Although our findings do not necessarily imply that superconductivity in e-doped LaOFeAs is due to an exotic mechanism, they clearly indicate that strong correlation effects beyond the LDA play an important role and must be included in any realistic description of this material.

**Technical Details:** For the atom-projected band and DOS plots in Fig. we employed the full-potential LAPW method as implemented in the Wien2k code. Calculations of phonon spectra, electron-phonon coupling and structural relaxations were performed using plane waves and pseudopotentials with QUANTUM-ESPRESSO. Whenever possible, we cross-checked the results given by the two codes and found them to be in close agreement; for consistency, we used the same GGA-PBE exchange-correlation potential in both cases.

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[22] We employed ultrasoft Vanderbilt pseudopotentials, with a cut-off of 40 Ryd for the wave-functions, and 320 Ryd for the charge densities. The $k$-space integration (electrons) was approximated by a summation over a 8 x 8 x 4 uniform grid in reciprocal space, with a Gaussian smearing of 0.02 Ryd for self-consistent cycles and relaxations; a much finer (16 x 16 x 8) grid was used for evaluating Densities of States (DOS) and electron-phonon linewidths. Dynamical matrices and electron-phonon linewidths were calculated on a uniform 4x4x2 grid in $q$-space; phonon dispersions and DOS were then obtained by Fourier interpolation of the dynamical matri-
ces, and the Eliashberg function by summing over individual linewidths and phonons. To check the effect of nesting on the e-ph linewidths, we also calculated selected \( \mathbf{q} \) points on a 882 grid, shown in Fig. 3.

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