

Is LaFeAsO_{1-x}F_x an Electron-Phonon Superconductor?

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In this Letter, we calculate the electron-phonon coupling of the newly discovered superconductor LaFeAsO_{1-x}F_x using linear response. For pure LaFeAsO, the calculated electron-phonon coupling constant $\lambda = 0.21$ and logarithmic-averaged frequency $\omega_{\text{ln}} = 206$ K give a maximum T_c of 0.8 K, using the standard Migdal-Eliashberg theory. For the F -doped compounds, we predict even smaller coupling constants. To reproduce the experimental T_c , a 5–6 times larger coupling constant would be needed. Our results indicate that electron-phonon coupling is not sufficient to explain superconductivity in the whole family of Fe-As-based superconductors, probably due to the importance of strong-correlation effects.

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The very recent report of superconductivity with the remarkable T_c of 26 K in LaFeAs[O_{1-x}F_x] [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, $M = \text{Mn, Fe, Co, and Ni}$, and Pn = P and As, synthesized in 1995 [2]. Superconductivity was first reported in LaFePO, with a relatively low T_c of ~ 7 K [3], and later in F -doped LaFeAsO, with a maximum T_c of 26 K at $x = 0.12$ (apparently pure LaFeAsO shows no superconductivity).

The first bulk measurements on a sample with $x = 0.1$ have shown that F -doped LaFeAsO has a relatively small in-plane coherence length ($\xi_{ab} = 81$ Å) 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] suggests the presence of nodes in the superconducting gap. All of these observations suggest a strong analogy with the high- T_c cuprates.

A recent local spin density functional calculation predicts that pure LaFeAsO 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 dynamical mean field theory calculation in the paramagnetic phase, including strong-correlation effects beyond local-density approximation (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 behavior [8]. These papers rule out standard electron-phonon (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 e -ph properties of LaFeAsO, using density functional perturbation theory [9,10]. Similar calculations, in conjunction with the Migdal-Eliashberg theory, reproduced the superconducting properties of many standard e -ph superconduc-

tors [10], including MgB₂ [11], with considerable accuracy. On the other hand, they fail dramatically in the high- T_c cuprates [12], where the local-density approximation is not sufficient to describe the strong local electronic correlations, and their interaction with phonons [13].

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

LaFeAsO crystallizes in a tetragonal crystal structure (space group 129), with $a = 4.035(3.996)$ Å, $c = 8.741(8.636)$ Å [14]; La and As atoms occupy $2c$ Wyckoff positions, with $z = 0.1415(0.1413)$ 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 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° (105.81°) or 113.5° (117.1°). 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 LaFeAsO are very similar to those of LaFePO [7,8,15]. 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 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

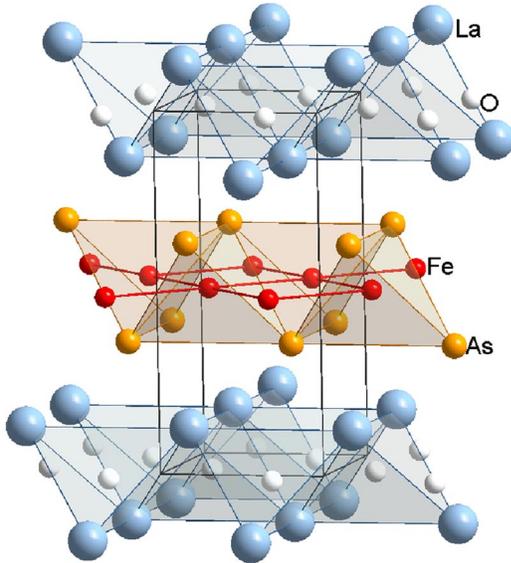


FIG. 1 (color online). Crystal structure of LaFeAsO.

field theory (see Fig. 2). Because of 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 subbands. d_{xy} states are inequivalent to d_{xz} , d_{yz} states, and the resulting 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 pseudogap opens in the electronic spectrum around 0.2 eV. As pointed out in previous publications, such a high DOS at the Fermi level drives the system close to a magnetic instability [7,8].

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. [7]). The plasma frequencies are strongly anisotropic ($\omega_{xx} = 2.30$ and $\omega_{zz} = 0.32$ 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 $\Gamma - Z$ line, as indicated by the small arrows in Fig. 2. A 1% percent compression of the tetrahedra along the c direction changes the splitting of the two d_{3z^2-1} bands by ~ 0.1 eV, driving one of them closer or further from the Fermi level. This explains why the position of the $3d_{z^2} - 1$ band, and the weight of the associated DOS, varies in literature, depending on the crystal structure used [7,8].

Figure 3 summarizes the e -ph properties of LaFeAsO; the results refer to pure LaFeAsO in the paramagnetic phase. It has been shown that the pure compound is close to a magnetic instability and to a metal-insulator transition

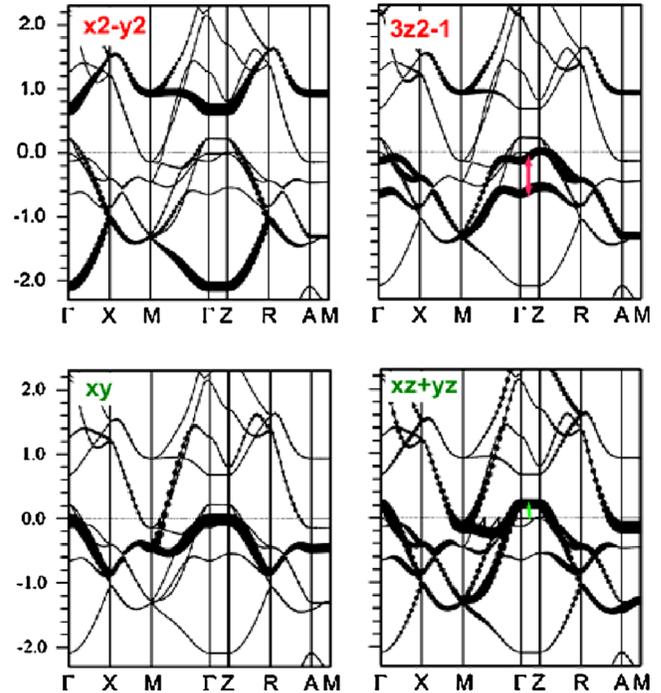


FIG. 2 (color online). Band structure of LaFeAsO, decorated with partial characters of the e_g (top) and t_{2g} (bottom) Fe- d bands. The orientation of the coordinate system is chosen so that Fe-Fe bonds are directed along the x and y axes; the zero of the energy coincides with the Fermi level. The arrows indicate the splitting induced by the elongation/shrinking of the Fe-As tetrahedra (see text).

due to electronic correlations [7,8]. Electron doping strongly suppresses the tendency to magnetism and reduces strong-correlation effects, and assuming a paramagnetic ground state is probably appropriate for the F -doped compound. Also, we checked by calculations in the virtual crystal approximation that the effect of F doping is well described by a rigid-band model, and the only effect of doping is a rigid-band shift of the Fermi level, in a region where the electronic DOS is lower (a 10% doping corresponds to a 40% reduction of the DOS). Therefore, the results for the undoped compound can be considered representative also for the electron-doped compound, provided that the reduced DOS is taken into account.

In the left panel of Fig. 3, we show the calculated phonon dispersion relations of LaFeAsO; our frequencies are in very good agreement with those of Ref. [7], where a slightly different crystal structure was used. In the middle panel of the same figure, we show the atom-projected phonon DOS. The spectrum extends up to 500 cm^{-1} ; the vibrations of O atoms are well separated in energy from those of other atomic species, lying at $\omega > 300 \text{ cm}^{-1}$. The vibrations of La, Fe, and As occupy the same energy range, and the eigenvectors have a strongly mixed character. Similarly to the electronic bands, the phonon branches have very little dispersion in the z direction. Analyzing

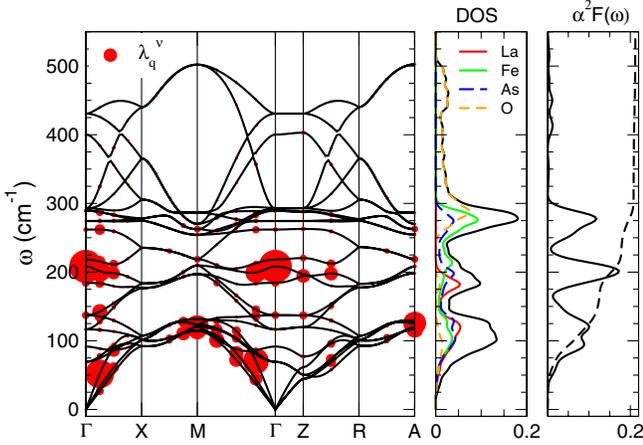


FIG. 3 (color online). Electron-phonon properties of LaFeAsO. Left: Phonon dispersion relations; the radius of the symbols is proportional to the partial mode λ of each phonon mode $\lambda_{\nu\mathbf{q}}$. For Γ and Z points, where the coupling diverges numerically, we use a different scaling factor. Middle: Atom-projected phonon DOS. The projection on in- and out-of-plane modes (not shown) does not show any clear separation between the patterns of vibration. Right: Eliashberg function $\alpha^2F(\omega)$ (solid line) and frequency-dependent e -ph coupling $\lambda(\omega)$ (dashed line).

the evolution of the phonon eigenvectors in the Brillouin zone (BZ) reveals that there is no clear separation between in- and out-of-plane vibrations, as often happens in layered compounds. The three major peaks in the phonon DOS at $\omega = 100, 200,$ and 300 cm^{-1} do not show a definite in-plane or out-of-plane character and cannot be easily traced back to a single vibration pattern. This complicates the interpretation of the Eliashberg spectral function $\alpha^2F(\omega)$ shown in the rightmost panel of Fig. 3:

$$\alpha^2F(\omega) = \frac{1}{N(0)} \sum_{nm\mathbf{k}} \delta(\varepsilon_{n\mathbf{k}}) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}) \sum_{\nu\mathbf{q}} |g_{\nu, n\nu\mathbf{q}}|, \quad (1)$$

together with the frequency-dependent e -ph coupling function $\lambda(\omega) = 2 \int_0^\omega d\Omega \alpha^2F(\Omega)/\Omega$.

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 of the phonon branches. Low-frequency phonons around 100 cm^{-1} provide $\sim 75\%$ of the total λ , due to the $1/\Omega$ factor in $\lambda(\omega)$, 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 σ bands, but the same applies also to more traditional superconductors, such as the A15, NbC, and even normal metals.

In LaFeAsO, all phonon modes give a comparable, small contribution to the total λ ; 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 LaFeAsO the only bands derived from directed bonds ($d_{x^2-y^2}$ 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 λ , i.e., to the partial contribution of each phonon mode to the total e -ph coupling: $\lambda_{\nu\mathbf{q}} \equiv \frac{1}{\pi N(0)} \frac{\gamma_{\nu\mathbf{q}}}{\omega_{\nu\mathbf{q}}^2}$, where $\gamma_{\nu\mathbf{q}}$ are the e -ph linewidths; summing $\lambda_{\nu\mathbf{q}}$ over the phonon branches ν and averaging on the BZ give the total e -ph coupling λ . 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 takes place.

The total e -ph coupling constant λ , obtained by numerical integration of $\lambda(\Omega)$ up to $\omega = \infty$, is 0.21; this, together with a logarithmically averaged frequency $\omega_{\text{ln}} = 205 \text{ K}$, and $\mu^* = 0$, gives $T_c = 0.5 \text{ K}$ as an upper bound for T_c , using the Allen-Dynes formula [16]. Numerical solution of the Eliashberg equations with the calculated $\alpha^2F(\omega)$ function gives $T_c = 0.8 \text{ K}$. To reproduce the experimental $T_c = 26 \text{ K}$, a 5 times larger λ would be needed, even for $\mu^* = 0$. Such a large disagreement clearly indicates that standard e -ph theory cannot be applied in LaFeAsO, in line with recent theoretical works which emphasize the role of strong electronic correlations and/or spin fluctuations [7,8].

The numerical uncertainty on the calculated value of λ , connected to limited sampling of the BZ in \mathbf{k} (electrons) or \mathbf{q} (phonons) space integration, is at most 0.1 and definitely not sufficient to raise λ to ~ 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 λ . 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 $T_c = 1.3 \text{ K}$.

In LaFeAsO, 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 λ is due to its extremely small matrix e -ph elements, connected to the strongly delocalized character of the Fe- d states at $\pm 2 \text{ eV}$ 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.

Since their electronic structure and phonon spectra depend very little on the chemical composition, our results can be considered representative for the whole class of Fe-As-based compounds.

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 [17]. Other interactions, repulsive in the s -wave channel but attractive in the d - or p -wave one, may increase T_c [18].

In conclusion, we have calculated the e -ph properties of the newly discovered superconductor LaFeAs[O_{1-x}F_x] 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 DOS. 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 of 5 too small to yield the experimentally measured T_c within the scope of the standard Migdal-Eliashberg theory.

The value $\lambda = 0.21$ in LaFeAsO is very close to those which have been estimated using LDA in the superconducting cuprates ($\lambda \sim 0.3$) [12]. Similarly, in this compound, superconductivity cannot be described using standard LDA calculations and the Migdal-Eliashberg theory. Although our findings do not necessarily imply that superconductivity in e -doped LaFeAsO is due to an exotic mechanism, they clearly indicate that strong-correlation effects beyond the LDA play an important role.

Technical details.—For the atom-projected band and DOS plots in Fig. 2, we employed the full-potential linear augmented-plane-wave method [19] as implemented in the WIEN2K code [20]. Calculations of phonon spectra, e -ph coupling, and structural relaxations were performed using plane waves and pseudopotentials with QUANTUM-ESPRESSO [21,22]. 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 generalized gradient approximation Perdew-Burke-Ernzerhof exchange-correlation potential in both cases [23].

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