



Electron–phonon properties of pnictide superconductors

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ABSTRACT

In this paper we discuss the normal and superconducting state properties of two pnictide superconductors, LaOFeAs and LaONiAs, using Migdal–Eliashberg theory and density functional perturbation theory. For pure LaOFeAs, the calculated electron–phonon coupling constant $\lambda = 0.21$ and logarithmic-averaged frequency $\omega_{ln} = 206$ K, give a maximum T_c of 0.8 K, using the standard Migdal–Eliashberg theory. Inclusion of multi-band effects increases the T_c only marginally. To reproduce the experimental T_c , a 5–6 times larger coupling constant would be needed. Our results indicate that standard electron–phonon coupling is not sufficient to explain superconductivity in the whole family of Fe–As based superconductors. At the same time, the electron–phonon coupling in Ni–As based compounds is much stronger and its normal and superconducting state properties can be well described by standard Migdal–Eliashberg theory.

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0. Introduction

Strong-coupling electron–phonon (EP) theory, also known as Migdal–Eliashberg (ME) theory, was developed in 1960s and 1970s to account for the physical properties of superconducting elemental metals and alloys, which could not be described by the weak-coupling BCS approach.

The electronic and phononic systems are described by a set of coupled diagrammatic equations (ME equations), which give a complete description of the normal and superconducting state, including the superconducting critical temperature. ME theory has been generalized to include multi-band and anisotropic coupling, magnetic and non-magnetic impurities, etc.; a review can be found in [1].

The biggest difficulty in 1960s and 1970s was extracting the EP coupling spectral function from the available experimental data, which involved some degree of approximation. In the last few years, it has become possible to calculate it completely *ab-initio* [2]. The combination of *ab-initio* calculations and ME theory has permitted to calculate the superconducting and normal state properties of many new and old materials with considerable accuracy [3]: the biggest success is probably represented by the two-gap superconductor MgB₂, with the record T_c of 40 K [4–6]. These methods, however, fail dramatically in more exotic superconductors, such as the high- T_c cuprates, where the key approximations

(weak electronic correlations, well separated phonon and electronic energy scales) break down [7,8].

In this paper, we analyze the possibility of applying ME theory to two newly-discovered pnictide superconductors, LaOFeAs and LaONiAs. The motivation of the application of the ME approach to Fe pnictides is connected with the rather large mass renormalization ($\lambda \approx 1 - 1.5$ in ARPES and de Haas–van Alphen effects, and slightly smaller $\lambda_{tr} \approx 0.6$ in transport properties) [9] as well as observed large isotope shift $\alpha_{Fe} \sim 0.4$ [10].

The results for the Fe compound were already presented in our previous publication [11], and we review them here, considering also the effect of multi-band coupling. We also decided to include new results for the Ni compound, LaONiAs, which is the only other member of the LaOMAs family (M = Mn, Fe, Co, Ni, Cu, Zn) [12] showing superconductivity, albeit with a much lower $T_c \approx 2.4 - 3.8$ K [13–15].

DFT calculations on other Ni pnictides [16,17] yielded values of the EP coupling constants ($\lambda = 0.58 - 0.72$), sufficient to reproduce their experimental T_c 's; [18,19] De Haas–van Alphen experiments on BaNi₂P₂ observed a renormalization of the band dispersion ~ 1.8 with respect to LDA calculations, which is in line with the above values of λ [20]. All these observations strongly suggest that Ni pnictides may be standard EP superconductors. In this work, we compare the available experimental data for LaONiAs (T_c , specific heat) with ME calculations, and we show that there is indeed a very good agreement. [13–15] To our knowledge, this is so far the most convincing proof so far that Ni pnictides are standard EP superconductors. The comparison of these results with those

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for LaOFeAs is very instructive. LaOFeAs has in fact a much smaller coupling constant λ , which is a factor 5 too low to reproduce the experimental $T_c = 26$ K [21], even considering multi-band effects. Similarly to the superconducting cuprates, LaOFeAs and Fe pnictides in general are much more “exotic” materials, where many-body effects may play an important role.

The exotic features of Fe pnictides (itinerant magnetism, structural transitions, unusual gap symmetry, etc.) are reviewed in detail in other contributions to this issue, and we will not treat them here, although in the last part of this paper we will discuss how they can affect our results.

This paper is organized as follows: in Section 1 we present the band structure and Fermi surface of the two compounds; in Section 2 we show the phonon dispersions and electron–phonon coupling calculated in Linear Response theory; in Section 3 we present the Migdal–Eliashberg results; in the last section we discuss our results in light of other experimental and theoretical works. The technical details of the density functional theory (DFT) calculations are given in Appendix A.

1. Electronic structure

LaOFeAs and LaONiAs crystallize in the ZrCuSiAs structure (space group 129); the primitive cell is tetragonal, La and As atoms occupy $2c$ Wyckoff positions, O and M atoms ($M = \text{Fe, Ni}$) occupy $2a$ and $2b$ Wyckoff positions.

The structure, depicted in Fig. 1, consists of alternating M–As and La–O layers. M and O atoms sit at the center of slightly distorted As and La tetrahedra; the As tetrahedra are squeezed in the z direction, so that there are two M–As–M angles (θ_1, θ_2), which are either larger or smaller than the regular tetrahedron value ($\theta_0 = 109.47^\circ$). M atoms form a square lattice; the M–M in-plane distance is $\sim 20\%$ larger than the M–As one. The relevant parameters of the structure for the two compounds are given in Table 1.

In this table we report both the experimental data, from Refs. [13,21], and the data that we obtained from a full DFT structural relaxation (Ref. [11] and present work), which we will use in the following calculations. As it was noticed by several authors in literature, in the Fe compound non-spin polarized DFT calculations tend to strongly overestimate the As tetrahedron deformation with respect to the experiment; the agreement is improved if spin polarization is allowed [22], which is normally interpreted as a sign of spin fluctuations [23–25]. On the other hand, in the Ni compound, the tetrahedral angles given by non-spin polarized DFT calculations are very close to those found experimentally (see Table 1).

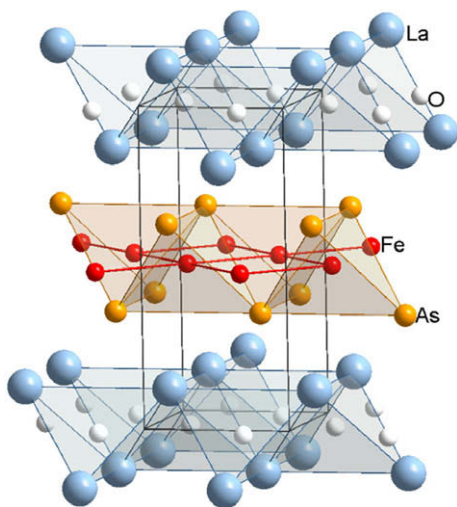


Fig. 1. Crystal structure of LaOFe(Ni)As, from Ref. [11].

Our band structures of LaOFeAs and LaONiAs are in very good agreement with literature results [11,22,26,28,29]. The most important difference between the two compounds is a ~ 1 eV shift of the Fermi level of the Ni(d^8) with respect to the Fe(d^6) compound, due to the different electron count. Measuring energies from the Fermi level of LaOFeAs, 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. The dominant contribution to the states in an energy window extending ± 2 eV around the Fermi level comes from the 10 M- d states, which hybridize with the As p states.

A blow-up of the band structure in this energy region, decorated with partial M d character, is shown in Figs. 2 and 3. The x, y axes are oriented along the M–M bonds. Due to the strong hybridization with As p states, the d bands do not split simply into a lower e ($d_{x^2-y^2}$ and d_{3z^2-1}) and higher t_2 manifold, as predicted by crystal field theory. The $d_{x^2-y^2}$ orbitals, which lie along the M–M in-plane bonds, due to hybridization are split into two subsets of flat bands of located at -2 and $+1$ eV. The d_{3z^2-1} bands have the most three-dimensional character and sit just below E_F . The t_2 bands, derived from d_{xy}, d_{xz} , and d_{yz} states, form a complicated structure centered at ~ -0.5 eV, and give the largest contribution to the Density of States (DOS) at the Fermi level.

The Fermi level of LaOFeAs 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. The resulting Fermi surface comprises two cylindrical hole pockets 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}, d_{xy} character.

The quasi-nesting between the hole and electron pockets leads to a peak in the magnetic susceptibility, and hence to an instability of the non-magnetic solution with respect to a striped antiferromagnetically (AFM) ordered phase. A third hole pocket centered around the Γ point is also present; its character (d_{3z^2-1} or d_{xy}) depends on the details of the calculations, and in particular on the deformation of the As tetrahedra [23]. The plasma frequencies are strongly anisotropic ($\omega_{xy}^{pl} = 2.30$, $\omega_z^{pl} = 0.32$ eV).

A similar blow-up of the band structure for the Ni compound is shown in Fig. 3. Due to the different electron count, the xz, yz hole pockets are completely full, and the Fermi surface contains two electron and one hole sheets, with a marked 2D character. Besides the elliptical xz, yz pocket, the second large electron sheet centered at the M point has a dominant $x^2 - y^2$ character; the same bands also forms small hole pockets around the X point of the Brillouin zone. The corresponding electronic states account for the directional in-plane bonds of the M planes.

The DOS is lower than in the Fe compound, $N(0) = 1.66$ st./eV spin, flat, and roughly particle-hole symmetric in an energy interval corresponding to 10% hole and electron doping. The Fermi velocities are on average higher than in LaOFeAs, and the resulting plasma frequency are larger and strongly anisotropic ($\omega_{xy}^{pl} = 4.49$ eV, $\omega_z^{pl} = 0.45$ eV).

The Γ -centered xz, yz hole pockets are completely full, and this suppresses the tendency to AFM order found in the Fe compound. In fact, we do not find any AFM solution, neither in the LSDA nor in the GGA, in agreement with previous calculations [29].

2. Electron–phonon properties

The main results of the linear response calculations for LaOFeAs and LaONiAs are shown in Table 2. In both cases we performed the calculations at zero doping in the non-magnetic (NM) phase. LaONiAs is non-magnetic and superconducting at zero doping; on the other hand, the ground state of undoped LaOFeAs, both in DFT [22] and experiment, is a striped antiferromagnetic order; doping suppresses magnetism and leads to superconductivity. Our NM

Table 1
Structural data of LaOFeAs and LaONiAs from experiment (Refs. [21] and [13]), and DFT (Ref. [11] and this work). Distances are in Å, angles in degrees; for a perfect tetrahedron, $\theta_1 = \theta_2 = 109.47^\circ$.

	a	c	z_{As}	z_{La}	d_{As-M}	d_{M-M}	θ_1	θ_2
LaOFeAs (exp)	4.035	8.741	0.6512	0.1415	2.41	2.85	107.5	113.5
LaOFeAs (th)	3.996	8.636	0.6415	0.1413	2.34	2.83	105.8	117.1
LaONiAs (exp)	4.123	8.1885	0.6368	0.1470	2.35	2.92	103.2	123.0
LaONiAs (th)	4.102	8.2886	0.6398	0.1423	2.36	2.90	104.0	121.1

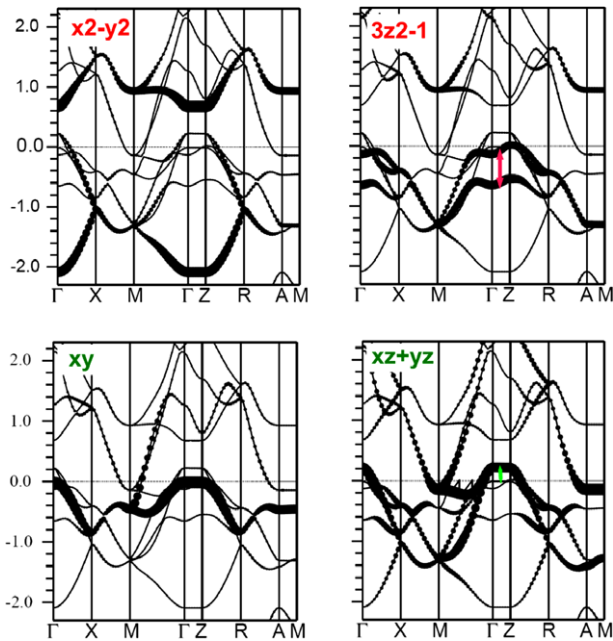


Fig. 2. Blow-up of the band structure of LaOFeAs around the Fermi level, decorated with partial e (red) and t_2 (green) Fe characters. From Ref. [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

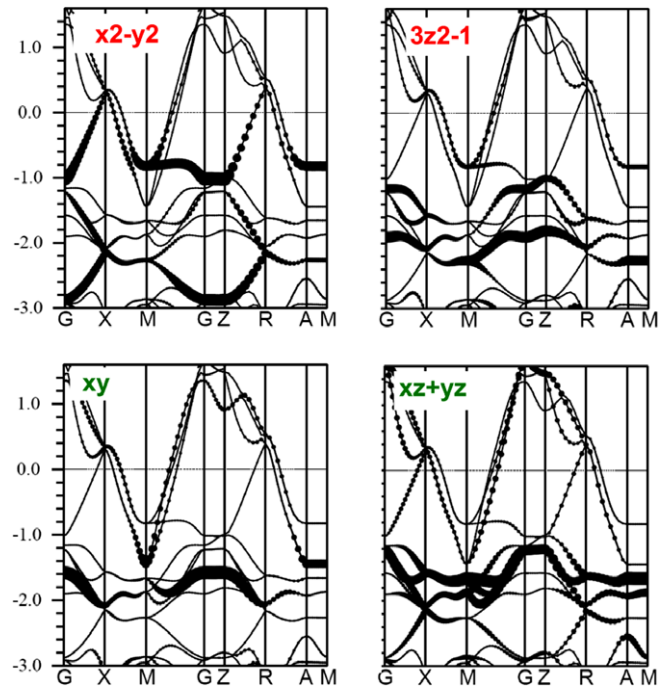


Fig. 3. Blow-up of the band structure of LaONiAs around the Fermi level, decorated with partial e (red) and t_2 (green) Ni characters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

calculations are thus meant as a model for doped, superconducting LaOFeAs, considering that the effect of doping in the virtual crystal approximation is roughly a rigid-band shift of the Fermi energy (E_F), which does not change the topology of the Fermi surface, but only the value of the DOS at E_F . It is important to point out that dynamic spin fluctuations, which have been argued to be present also in the superconducting Fe samples, are not included in this calculation, but would require going beyond the DFT level. We will discuss this issue in more detail in the final section of this work.

In the two top panels of Fig. 4 we show the atom-projected phonon DOS (PDOS) of LaOFeAs (top) and LaONiAs (bottom). Both spectra extend up to 65 meV, and have a rather similar shape. The vibrations of O atoms are well separated in energy from those of other atomic species, lying at $\omega > 40$ meV. The vibrations of La, Fe(Ni) and As occupy the same energy range, and the eigenvectors have a strongly mixed character. Similarly to the electronic bands, the phonon branches (not shown) have very little dispersion in the z direction. Analyzing 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 it often happens in layered compounds. The three major peaks in the PDOS at $\omega = 10, 20$ and 30 meV do not show a definite in-plane or out-of-plane character, and cannot be easily traced back to a single vibration pattern. Their energy is shifted down by $\sim 20\%$ when going from Fe to Ni, mostly due to EP softening.

The EP coupling of LaONiAs ($\lambda = 0.72$) is in fact much larger than in LaOFeAs ($\lambda = 0.21$), as shown in the two lower panels of Fig. 4.

Here, we plot the two Eliashberg spectral functions $\alpha^2F(\omega)$, together with the frequency-dependent EP coupling function $\lambda(\omega)$:

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

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

where $g_{v,nk,mk}$ are the bare DFT matrix elements, *i.e.* they do not include many-body effects. A comparison of the Eliashberg function with the PDOS shows that, apart from the fact that in both systems the high-lying O modes show very little coupling to electrons, there are important differences in the shape and size of $\alpha^2F(\omega)$ between the Fe and the Ni compound. In fact, in LaOFeAs there is an almost perfect proportionality between the PDOS and the $\alpha^2F(\omega)$, whereas in LaONiAs the coupling to the two lowest peaks of the PDOS is strongly enhanced.

A perfect proportionality between the Eliashberg function and the PDOS (LaOFeAs) implies that there are no patterns of vibration with a dramatic effect on the electronic states at the Fermi level. In good EP superconductors, on the other hand, 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

Table 2

Electron–phonon properties of Fe and Ni superconductors calculated from density functional perturbation theory. The results in the first two rows are from Ref. [11] and this work. The T_c values in the first column ($T_{c,th}$) are obtained using $\mu^* = 0.12$ and Allen–Dynes formula (Eq. 3); number in parentheses correspond to the full numerical solution of Migdal–Eliashberg equations, given in Section 3. For comparison, in the last three rows we also report literature data on FeSe, LaONiP and BaNi₂As₂ from Refs. [27,16,17].

	$N(0)eV^{-1}f u^{-1}$	$\omega_{ky}^{pl}(eV)$	$\omega_z^{pl}(eV)$	$\omega_{in}(K)$	λ	$\gamma_0(mJmol^{-1} K^{-2})$	$T_{c,th}(K)$	$T_c^{exp}(K)$
LaOFeAs	2.1	2.30	0.23	205	0.21	4.95	0.0 (0.0)	26 [21]
LaONiAs	1.64	4.49	0.45	96	0.72	3.86	2.9 (3.8)	2.4 [13], 3.8 [14]
FeSe	1.9	–	–	163	0.17	4.48	0.0	18
LaONiP	1.41	–	–	162	0.58	3.32	2.6	3
BaNi ₂ As ₂	1.78	–	–	105	0.76	4.20	3.8	0.7

EP interaction between strongly directed orbitals [30]. In the previous section, we have seen that, due to the different electron count, the $d_{x^2-y^2}$ states, which account for directed Fe–Fe bonds, and thus experience a strong coupling to the low-energy Ni–As modes, sit at the Fermi level in LaONiAs, and are unoccupied in LaOFeAs.

As it can be seen by comparing the two lower panels of Fig. 4, the coupling of the electronic states at the Fermi level to the low-energy part of the phonon spectra of LaONiAs is in fact approximately 4 times larger than in LaOFeAs. Given that the electronic DOS of LaONiAs is 25% lower, the coupling of its low-energy phonons to the electronic states at the Fermi level must be 5 times larger.

The different EP coupling of LaONiAs and LaOFeAs derives from the character of the electronic states at the Fermi energy. Therefore, it should be a rather general property of the Fe and Ni families of pnictide superconductors which, apart from minor differences due to chemistry and structure, share the same band structure.

In fact, as we show in Table 2, the calculated EP coupling constants in Ni compounds ($\lambda \approx 0.58 - 0.76$) [16,17] are always 3–4 times larger than in Fe-based materials ($\lambda \approx 0.17 - 0.21$)

[11,26,27]. This has important implications on the possible pairing mechanism for superconductivity in the two classes of materials. We can get an estimate of T_c due to EP coupling using Allen–Dynes formula [31]:

$$T_c = \frac{\langle \omega_{ln} \rangle}{1.2} \exp \left[\frac{-1.04(1 + \lambda)}{\lambda - (1 + 0.62\lambda)\mu^*} \right], \quad (3)$$

For $\mu^* = 0.12$, this gives $T_c < 0.01$ K ($\omega_{ln} = 205$ K) for LaOFeAs and $T_c = 2.9$ K for LaONiAs ($\omega_{ln} = 96$ K).

To reproduce the experimental ($T_c = 26$ K) of LaOFeAs, a five times larger λ would be needed, even for $\mu^* = 0$. On the other hand, the DFPT results seem to nicely explain the T_c of LaONiAs.

In the next section, we will calculate in more detail the normal and superconducting state properties of 10% F-doped LaOFeAs and LaONiAs using the full ME theory, and compare the results with available experimental data. We will use the Eliashberg functions $\alpha^2F(\omega)$ we calculated for the undoped materials. This is justified by the fact that, in both cases, doping does not modify either the topology of the Fermi surface or the character of the states at the Fermi level, but merely changes the value of the DOS at E_F . As discussed at the beginning of this section, the $\alpha^2F(\omega)$ of undoped LaOFeAs gives an upper bound to the EP T_c of LaOFeAs; in LaONiAs, where the DOS is basically flat in a doping range corresponding to 20% hole and 10% electron doping, we expect that the $\alpha^2F(\omega)$ of the undoped material is a good approximation for the 10% doped compound.

3. Superconducting properties

(a) *LaFeAsO_{0.9}F_{0.1}*

In principle, multi-band and/or anisotropic coupling could provide the missing factor 5 in the coupling missing to explain T_c similar to the multi-band superconductivity in MgB₂ (see e.g., Refs. [5,6]); however this is very unlikely because this would require a very anisotropic distribution of the EP coupling [32]. Definitely, the iron pnictides are multi-band superconductors with hole and electron bands which are well separated in momentum space. To analyze this possibility we split the electron–phonon interaction (EPI) in Eq. (1) over electron and hole pockets on the Fermi surface, obtaining the band-decomposed superconducting Eliashberg functions:

$$\alpha_{ij}^2(\omega)F_{ij}(\omega) = \frac{1}{N_i(0)} \sum_{\mathbf{k}, \mathbf{k}', \nu} |g_{\mathbf{k}, \mathbf{k}'}^{ij, \nu}|^2 \times \delta(\epsilon_{\mathbf{k}}^i) \delta(\epsilon_{\mathbf{k}'}^j) \delta(\omega - \omega_{\mathbf{k}-\mathbf{k}'}^\nu), \quad (4)$$

where $N_i(0)$ is the partial DOS per spin at the Fermi energy of the i th sheet of the Fermi surface, $g_{\mathbf{k}, \mathbf{k}'}^{ij}$ is the EPI matrix element. These functions, shown in Fig. 5, determine the superconducting properties and thermodynamical properties like electronic specific heat and de Haas–van Alphen mass renormalizations. In contrast to MgB₂, in LaOFeAs the matrix of coupling constant is practically uniform:

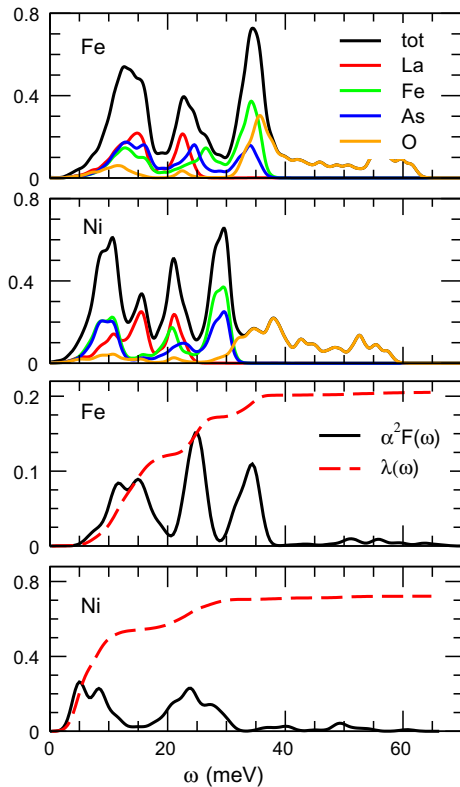


Fig. 4. From top to bottom: Partial PDOS (Fe, Ni), Eliashberg functions and frequency-dependent electron–phonon coupling constant $\lambda(\omega)$ (Eq. 1 and 2) for LaOFeAs and LaONiAs, calculated within Density Functional Perturbation Theory (DFPT).

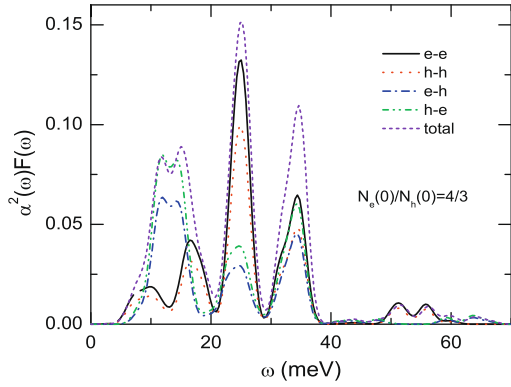


Fig. 5. The decomposition of the Eliashberg function on the *intra*band and *inter*band interactions; the ratio between hole and electron DOS is obtained from a 2nd order fit of the band structure around E_F .

$$\lambda = \begin{pmatrix} 0.111 & 0.093 \\ 0.124 & 0.083 \end{pmatrix},$$

while the characteristic logarithmic frequencies are different ($\omega_{\text{ln}}^{\text{intra}} = 214$ K, and $\omega_{\text{ln}}^{\text{inter}} = 180$ K). The small difference in the elements of the matrix λ leads to a non-drastring difference between the maximal eigenvalue and the EPI averaged over bands. As a result we get slightly larger value of $T_c \approx 1.5$ K, for $\mu^* = 0$ which is much lower than the observed value $T_c = 26$ K. In view of the above result, we do not pursue the ME study of LaOFeAs further. Other interactions, repulsive in the *s*-wave channel but attractive in the *d*- or *p*-wave one (e.g. spin fluctuations or the direct Coulomb interaction), may increase T_c [26].

(b) $\text{LaNiAsO}_{0.9}\text{F}_{0.1}$

LaONiAs is superconducting with $T_c \approx 2.4 - 3.8$ K when hole (Sr) or electron (F) doped. The phase diagram is roughly symmetric, in agreement with the flat DOS predicted by DFT in this doping interval. In this paragraph, we apply ME theory to $\text{LaNiAsO}_{0.9}\text{F}_{0.1}$, for which we could find the most complete set of experimental data in literature [14].

The calculated Eliashberg spectral function $\alpha^2(\omega)F(\omega)$ shown in Fig. 4, with a total $\lambda = 0.72$, yields the experimental $T_c = 3.8$ K, with a Coulomb pseudopotential of $\mu^* = 0.12$ (slightly higher then by using the Allen–Dynes expression). We fix $\mu^* = 0.12$ in the following discussion. The calculated gap at zero temperature $\Delta(0)$ is 6.97 K, which gives a ratio $2\Delta/T_c = 3.7$, higher than the BCS value.

We now wish to investigate the temperature dependence of the specific heat, which yields valuable information on the size and nature of the EP coupling.

In a single-band model with a strong (intermediate) EPI, in the normal state and in the adiabatic approximation the electronic contribution to the specific heat is determined from the Eliashberg function $\alpha^2(\omega)F(\omega)$ by the expression [33]:

$$C_N^{\text{el}}(T) = (2/3)\pi^2 N(0)k_B^2 T \times \left[1 + (6/\pi k_B T) \int_0^\infty f(\omega/2\pi k_B T) \alpha^2(\omega)F(\omega) \omega \right], \quad (5)$$

where $N(0)$ is a bare DOS per spin at the Fermi energy. The kernel $f(x)$ is expressed in terms of the derivatives of the digamma function $\psi(x)$

$$f(x) = -x - 2x^2 \Im \psi'(x) - x^3 \Re \psi''(x). \quad (6)$$

At low temperatures the specific heat has the well known asymptotic form: $C_N^{\text{el}}(T \rightarrow 0) = (1 + \lambda)\gamma_0 T$, where λ is the electron–phonon coupling constant, and $\gamma_0 = 2\pi^2 k_B^2 N(0)/3$ is the spe-

cific heat coefficient for non-interacting electrons. At higher temperatures the specific heat differs from this trivial expression. Below T_c the difference in free energies, F_N and F_S , of the superconducting and normal state is given by:

$$-\frac{F_N - F_S}{\pi N(0)T} = \left\{ \sum_{n=-\omega_c}^{\omega_c} |\omega_n| (Z^N(\omega_n) - 1) - \frac{2\omega_n^2 (Z^S(\omega_n)^2 - 1) + \varphi_n^2}{|\omega_n| + \sqrt{\omega_n^2 (Z^S(\omega_n))^2 + \varphi_n^2}} + \frac{\omega_n^2 Z^S(\omega_n) (Z^S(\omega_n) - 1) + \varphi_n^2}{\sqrt{\omega_n^2 (Z^S(\omega_n))^2 + \varphi_n^2}} \right\}, \quad (7)$$

where $Z(\omega_n)$ is a normalization factor, $\varphi_n = \Delta_n/Z(\omega_n)$ is an order parameter, and Δ_n is the gap function (see the derivations in [6] and [34]).

The specific heat at temperature, T , is then calculated according to:

$$\Delta C_{\text{el}}(T) = T \partial^2 (F_N - F_S) / \partial T^2. \quad (8)$$

The specific heat jump $\Delta C_{\text{el}}(T_c)$ at $T = T_c$ is determined by the coefficient $\beta = T_c \Delta C_{\text{el}}(T_c)/2$ of a second order expansion $F_N - F_S = \beta t^2$, where $t = (T_c - T)/T_c$.

For the comparison with experiment we have considered the data in Ref. [14]. The anomaly clearly visible at T_c in the zero-field data is suppressed by a magnetic field of 10 T. In Fig. 6 the difference $\Delta C_p = C_p(0 \text{ T}) - C_p(10 \text{ T})$ is displayed as symbols. The specific heat in $\text{LaNiAsO}_{0.9}\text{F}_{0.1}$ was calculated using the isotropic spectral Eliashberg function $\alpha^2(\omega)F(\omega)$ shown in Fig. 4. The calculated specific heat at T_c is $\gamma^N(0) = 1.72\gamma_0 = 6.64 \text{ mJ/mol K}^2$ with $\gamma_0 = 3.86 \text{ mJ/mol K}^2$ from the band structure calculations. This value is close to the experimental one of 6.14 reported in Ref. [14] (see Ref. [35]). The specific heat jump at T_c equals $\Delta C/T_c = 11.1 \text{ mJ/mol K}^2$, which is comparable the experimental values [14]. This gives $\Delta C/(\gamma^N(0)T_c) \approx 1.67$ slightly larger than the BCS value of 1.43 which corresponds to the intermediate coupling. To estimate the specific heat jump we can also apply the semiempirical expression by Carbotte [36].

$$\Delta C/T_c = 1.43\gamma_0(1 + \lambda) \left[1 + \left(\frac{T_c}{\omega_{\text{ln}}} \right)^2 \ln \left(\frac{\omega_{\text{ln}}}{3T_c} \right) \right].$$

With $\omega_{\text{ln}} = 96$ K and with $T_c = 3.8$ K, we have $\Delta C/T_c = 11.2 \text{ mJ/mol K}^2$, which compares well with the full numerical solution. The difference $\Delta C_{\text{el}}(T) = C_{\text{el}}^S(T) - C_{\text{el}}^N(T)$, shown in Fig. 6 as solid line, shows a very good agreement with the experimental data. We would like to emphasize here that no fitting is involved in the theoretical calculations. The only free parameter which is

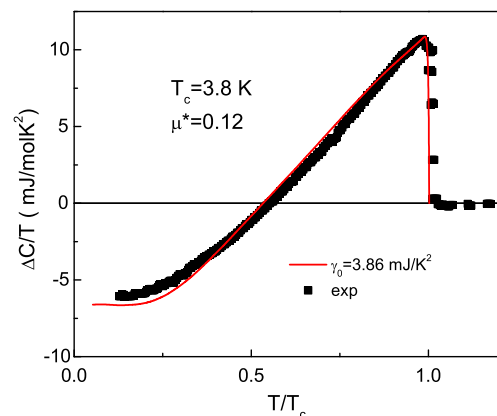


Fig. 6. The specific heat of the $\text{LaNiAsO}_{0.9}\text{F}_{0.1}$ compound. The solid (red) line shows results of the calculations. Black dots correspond to experimental results from Ref. [14]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the Coulomb matrix element μ^* , which was determined by the experimental T_c .

Here, we have to point out that the specific heat jumps in multi-band systems (or other anisotropic ones) is sufficiently smaller than in one-band superconductors (see discussions in [6] and [34], and some criteria in [37]). These results show that T_c and the specific heat in $\text{LaNiAsO}_{0.9}\text{F}_{0.1}$, in contrast to $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$, can be described in the framework of the standard single-band approach without the need of exotic mechanisms.

4. Discussion

To summarize the results of the previous sections, we have found that linear response calculations of the electron–phonon coupling yield rather different results for the two superconducting members of the LaOMAs family of pnictide superconductors.

For the Fe compound the value of the total EP coupling constant $\lambda = 0.21$ is much lower than in normal EP superconductors (for example, $\lambda = 0.44$ in Al, where T_c is 1.3 K), and even the inclusion of multi-band effects cannot explain the $T_c = 26$ K observed in doped samples.

For the Ni compound the coupling constant is much higher ($\lambda = 0.72$); its normal and superconducting state properties can be well described by standard, single-band Migdal–Eliashberg theory. The values of the gap ratio $2\Delta/T_c = 3.7$ and specific heat jump $\Delta C/\gamma^N(0)T_c = 1.67$ are larger than what predicted by BCS theory (3.52 and 1.43), respectively.

The picture that emerges from our calculations is that of a family of rather standard EP superconductors (Ni-based), opposed to a family of “exotic” superconductors (Fe-based), which is supported by several experimental evidences.

The most important issue is the magnetic ground state of the superconducting samples. The Ni parent compounds are standard metals, which superconduct at low $T < 5$ K [13–15,19,18,20]¹; doping (holes or electrons) does not change T_c or normal state properties dramatically. The calculated EP coupling constants $\lambda = 0.58 - 0.76$ [16,17] can well explain the experimental T_c and, as we have shown in the previous section, also thermodynamic properties. To further support the picture of conventional superconductivity, recent de Haas–van Alphen experiments on an other Ni pnictide, BaNi_2P_2 , observe a band structure which is in close agreement with DFT calculations; the average effective mass renormalization is ~ 1.8 , which implies an EP coupling constant $\lambda = 0.8$, in good agreement with the values of λ for other Ni pnictides. [20]. Data on the Ni and As isotope effect on the Ni pnictide, which would be the ultimate confirmation of this picture, are unfortunately still missing.

On the other hand, in the Fe compounds superconductivity only appears by doping a parent compound which is an AFM metal. At the time when our calculations presented in Ref. [11] were performed, the only available experimental data showed that doping suppressed the static AFM order in the superconducting samples. [21] Therefore, we assumed that, as in the Ni superconductors, also in Fe superconductors the normal state is non-magnetic.

In the last few months, experiments have shown that the ground state of the superconducting samples may also be magnetic, but with fluctuating (dynamic) moments. Such an arrangement is not describable by DFT theory, therefore it is not possible to estimate what its effect on the EP coupling would be. For a more complete discussion of this subject, see the review by Mazin and Schmalian in this issue.

It is also hard to compare our results with experimental data. There are no direct measurements of the EP coupling in literature, although some experiments (ARPES, penetration depth, specific

heat) indicate some retarded electron–boson interaction, with a coupling constant $\lambda^B \approx 0.5 - 1.5$; however, the total coupling could be due to other bosonic excitations.

On the other hand, a few measurements of phonon spectra are available in literature [38–43]. In general, there is a good agreement between experimental phonon frequencies and non-spin polarized calculations, except for the intermediate frequency Fe–As (and As–As) modes, which are lower in experiment than in calculations. See for example Ref. [39], where Inelastic Neutron Scattering data are compared to our PDOS. An empirical way to reconcile experiment and theory, by reducing the Fe–As force constant, was proposed in Ref. [40]. It was later shown that the inclusion of a static AFM order leads indeed to a softening the Fe–As spring constant, and improves the agreement of the predicted crystal structure and phonon frequencies with experiment [44]; however, this cannot explain the softening of c-polarized As modes, which form a distinct peak at 20 meV, at an energy 20% lower than predicted by calculations, which has been observed both in 1111 and 122 samples, and has been attributed to anomalous e–ph coupling [41,43].

It was realized very early that Fe pnictide show a strong magneto-elastic coupling between Fe moments and As out-of-plane modes [11,28,22]; in Ref. [45] it was proposed that this leads to an increased EP coupling. In principle, also many-body effects could increase the coupling constant beyond the LDA value.

In conclusion, on the basis of our results we can exclude that standard EP coupling theory alone can cause the observed T_c in Fe pnictides; however, this does not mean that the phonons play no role in the superconducting pairing, as they might enhance or reduce the pairing due to other mechanisms. If this is the case, it is not surprising to observe a finite Fe isotope effect on T_c .

On the other hand, LaONiAs represents a nice example of a single-gap, strong-coupling EP superconductor. Measurements of Ni and As isotope effects, which could definitely confirm this picture, are highly desirable.

It is important to stress that the difference between the two compounds can be traced back essentially to a different filling of the same complicated, non-magnetic band structure, which derives from a non-trivial hybridization between M and pnictogen atoms.

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Appendix A. Computational details

For the atom-projected band and DOS plots in Figs. 2 and 3 we employed the full-potential LAPW method [46] as implemented in the Wien2k code [47]. Calculations of phonon spectra, EP coupling and structural relaxations were performed using planewaves and pseudopotentials with QUANTUM-ESPRESSO [48]. We employed ultrasoft Vanderbilt pseudopotentials [49], with a cut-off of 40 Ryd for the wave-functions, and 320 Ryd for the charge densities. The \mathbf{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 0.02 Ryd for self-consistent cycles and relaxations; a much finer ($16 \times 16 \times 8$) grid was used for evaluating DOS and EP linewidths. Dynamical matrices and EP linewidths were calculated on a uniform $4 \times 4 \times 2$ grid in \mathbf{q} -space; phonon dispersions and DOS were then obtained by Fourier interpolation of the dynamical matrices, and the Eliashberg function by summing over individual

¹ A possible SDW transition has been observed at ~ 66 K in BaNi_2As_2 in Ref. [19].

linewidths and phonons. To check the effect of nesting on the EP linewidths, we also calculated selected \mathbf{q} points on a $8 \times 8 \times 2$ grid.

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 [50].

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