Anomalous electron-phonon interaction in doped LaFeAsO: First-principles calculations

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We present first-principles calculations of the atomic and electronic structure of electron-doped LaOFeAs. We find that whereas the undoped compound has an antiferromagnetic arrangement of magnetic moments at the Fe atoms, the doped system becomes nonmagnetic at a critical electron concentration. We have studied the electron-phonon interaction in the doped paramagnetic phase. For the A_{1g} phonon, the separation between the As and Fe planes induces a noncollinear arrangement of the Fe magnetic moments. This arrangement is antiparallel for interactions mediated by As and perpendicular for Fe-Fe direct interactions, thus avoiding frustration. This coupling of magnetism with vibrations induces anharmonicities and an electron-phonon interaction much larger than in the pure paramagnetic case. We propose that such enhanced interactions play an essential role in superconducting compounds close to an atiferromagnetic phase transition.

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I. INTRODUCTION

Very recently, Kamihara *et al.*[1,2] reported a new family of Fe based compounds that are superconducting when doped. All these *R*OFeAs (*R*=La, Sm, etc.) materials are formed by FeAs layers separated by insulating rare-earth-oxide layers. They are superconducting when doped with electrons by substituting O for F, whereas the parent compounds are antiferromagnetic (for a recent review see Ref. 3). The superconducting critical temperature T_c is as high as 50 K.[4] The phase diagram has been well established experimentally both as a function of doping[5,6] and pressure.[7] The variation and ordering of the antiferromagnetic phase with temperature have been measured with neutron diffraction.[8] The phonon modes have been determined by Raman spectroscopy.[9] Photoemission experiments, and first-principles calculations, have revealed a Fermi surface with two electron pockets and two hole pockets.[10]

The precise mechanism responsible for the superconductivity has not been yet established. Theoretical calculations[11] rule out electron-phonon interaction to be the only pairing mechanism. Electron-phonon interaction in the paramagnetic phase can only account for a maximum T_c of 0.8 K.[11] Other calculations[12] also rule out phonon mediated superconductivity. The magnetic structure of the parent compounds is well established experimentally although, from the theoretical point of view, there are some discrepancies, between different calculations and with the experimental results, in the magnitude of the magnetic moment at the Fe atoms.[13]

II. METHODOLOGY

In this work we present first-principles calculations to analyze in more detail the electron-phonon interaction in the doped paramagnetic phase. The density functional[14,15] calculations are performed using the SIESTA code[16,17] which uses localized orbitals as basis functions.[18] In our calculation we use a double ζ polarized basis set. We use nonlocal norm conserving pseudopotentials and a local density approximation (LDA) for the exchange and correlation functional. The calculations are performed with stringent criteria in the electronic structure convergence (down to 10^{-5} in the density matrix), Brillouin zone sampling (up to 180 00 *k* points), real space grid (energy cutoff of 500 Ry), and equilibrium geometry (residual forces lower than 10^{-2} eV/Å). Due to the rapid variation in the density of states at the Fermi level, we used a special smearing method.[19]

III. DOPING EFFECT ON THE MAGNETIC ORDER

We first calculate the variation in the total energy with the lattice parameter for various possible magnetic configurations. In Fig. 1 we show the results for two possible antiferromagnetic configurations in the Fe atoms: direct antiferromagnetic ordering between nearest neighbor Fe atoms (AF0) and antiferromagnetic Fe-Fe interaction mediated by As (AF1). We find that, at the calculated equilibrium lattice constant (3.97 Å), the ground state has AF1 magnetic order. Its energy difference with AF0 (which is non magnetic at that lattice constant) is 26 meV/f.u. Ferromagnetism and other noncollinear magnetic configurations are found to be unstable. The AF1 magnetic moment is $1.3\mu_B$/Fe atom, in reasonable agreement with previous all-electron density functional calculations.[20,21] This calculated value is larger than the $0.36\mu_B$/atom found in neutron diffraction experiments,[8] possibly due to neglected spin fluctuations.[13] In the equilibrium configuration the direct Fe-Fe distance is 2.81 Å and the distance between the As and the Fe planes is 1.26 Å in good agreement with previous calculations and with experiments.[8]

In order to simulate the doped phase we have added electrons to the system while keeping the charge neutrality by adding a uniform positive charge background. As shown in Fig. 2, the magnetic moments decrease with electron doping, and they disappear above a critical concentration. This critical value (0.26 electron/f.u.) is larger than the experimental one, probably due to the overestimation of the magnetic moment in the undoped phase. From the structural point of view, the main effect of electron doping is the decrease in the distance between the As and Fe planes. For instance, in the paramagnetic phase, with 0.275 extra electrons, the compression is 0.02 Å. This compression, added to the filling of the

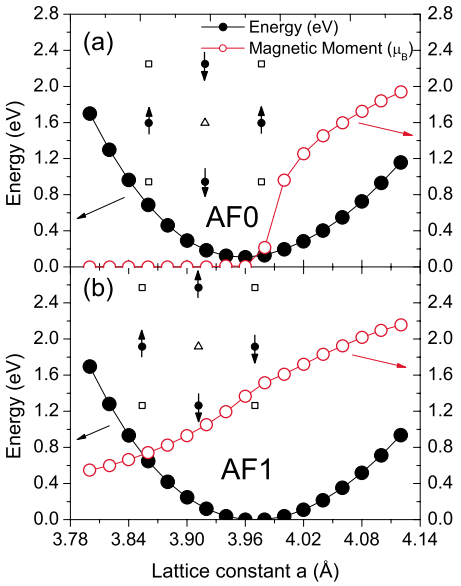

FIG. 1. (Color online) Variation in total energy (left scale) and magnetic moment of Fe atoms (right scale) with the lattice constant a in two different antiferromagnetic arrangements of LaOFeAs: (a) direct Fe-Fe antiferromagnetic order (AF0) and (b) As-mediated antiferromagnetic order (AF1). The zero of energy is at the AF1 minimum. The orientations of the Fe magnetic moments in each configuration are indicated in the insets, where squares and triangles stand for As atoms above and below the plane of Fe atoms. The total energy is for a $(\sqrt{2}a \times \sqrt{2}a \times c)$ supercell.

Fe d levels and the shift of the Fermi energy to a region with lower density of states, is responsible for the disappearance of magnetism. Figure 2(b) shows that the extra charge goes mainly to the As-Fe-As layer, as anticipated.[22]

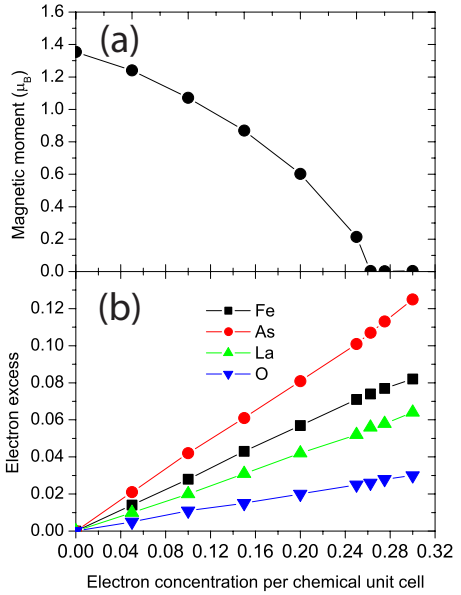

FIG. 2. (Color online) Calculated effects of electron doping in the AF1 magnetic configuration of LaOFeAs (see text). (a) Magnetic moment per Fe atom. (b) Distribution of the extra charge among the different atoms.

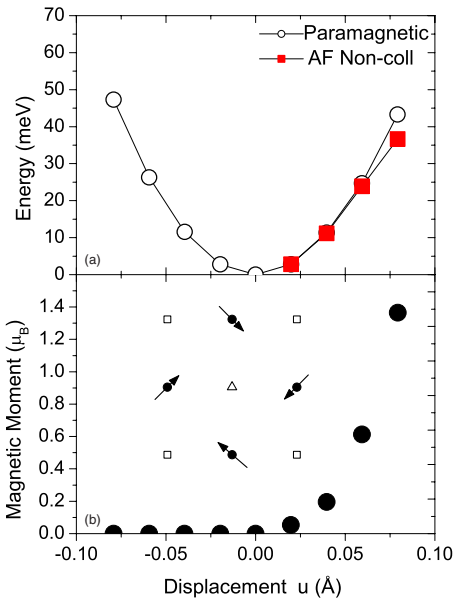

FIG. 3. (Color online) Variation in energy and magnetic moment with the amplitude u of the A_{1g} phonon at Γ (vibration of As atoms perpendicular to the Fe plane) for a doping of 0.275 electrons/f.u. (a) Energy per f.u. in the paramagnetic and noncollinear magnetic configurations. (b) Noncollinear magnetic moment of the Fe atoms. Their orientations are indicated in the inset, where squares and triangles stand for As atoms above and below the Fe plane.

IV. ELECTRON-PHONON INTERACTION

To address the electron-phonon interaction in this system, we have considered the symmetric out-of-plane FeAs A_{1g} mode at $k_{\|}=0$, in which the Fe atoms remain fixed whereas the As atoms move perpendicularly to the FeAs layers, expanding and compressing the Fe-As bonds. Figure 3 shows the calculated total energy and magnetic moment, as a function of the expansion (positive u) or compression (negative u) of the Fe-As interplanar distance, for an extra concentration of 0.275 electron/f.u. Several points are worth mentioning: (i) Expansion of the Fe-As distance induces magnetism in the Fe atoms. (ii) In this case the arrangement of the magnetic moments at the Fe atoms is noncollinear, such that the As-mediated interaction remains antiferromagnetic, while there is no longer magnetic frustration for the direct Fe-Fe interaction, as in the AF1 order. A similar result has been obtained using the unrestricted Hartree-Fock approximation and Landau theory in a Hubbard-type model Hamiltonian.[23] (iii) Compression of the Fe-As planes does not induce magnetism, and this asymmetry makes the vibration strongly anharmonic. The energy per f.u. can be fitted by the fourth-order polynomial $E(u)=\hbar\omega(x^2-0.107x^3-0.064x^4)$, where $\hbar\omega=29.0$ meV is the calculated phonon energy, $x \equiv u/u_0$, and $u_0=0.062$ Å. Thus, the restoring forces are +0.91 and −0.68 eV/Å for $u=-0.06$ and +0.06 Å, respectively. (iv) The magnetic moments appear even for small phonon amplitudes, such that $E(u) \leq \hbar\omega$ $(u \leq u_0)$. (v) For positive u, the noncollinear solution is less than ~1 meV lower than the AF1 configuration, which has very similar magnetic moments. (vi) A similar, although weaker, effect has been ob-

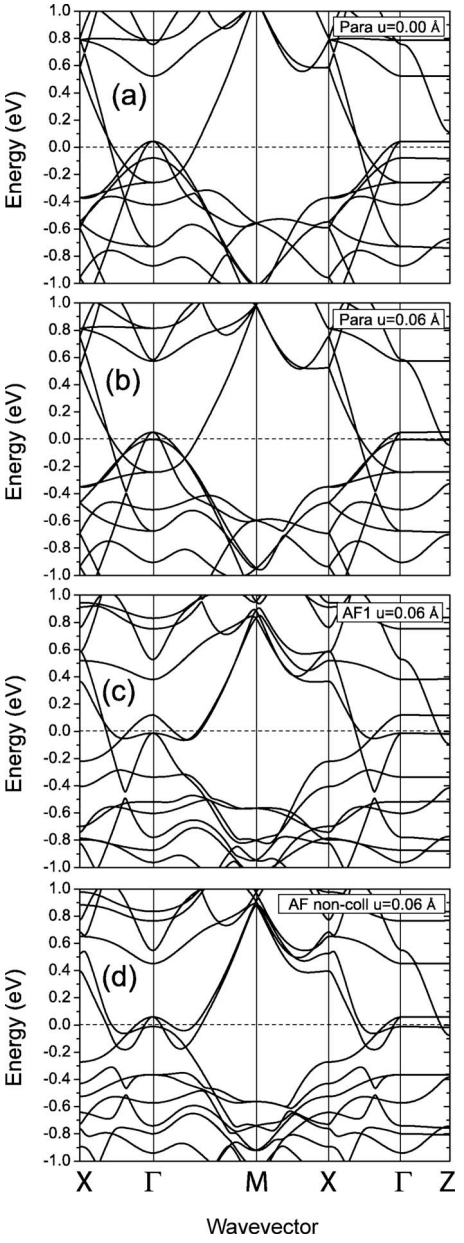

FIG. 4. Electronic band structure for LaOFeAs, doped with 0.275 electrons/f.u., for different magnetic configurations (paramagnetic, AF1, and AF noncollinear, see text) and vibration displacements u of the A_{1g} phonon at Γ. The Brillouin zone is for the $(\sqrt{2}a \times \sqrt{2}a \times c)$ supercell. The zero of energy is at the Fermi level.

tained in the calculation of the asymmetric A_{2u} mode.

Next we study how the A_{1g} vibration affects the electronic structure in detail. Figure 4 shows the calculated band structure, with an electron doping of 0.275, for different magnetic states and vibration displacements. The electron and hole pockets appear both at Γ since the calculations were performed with a $(\sqrt{2}a \times \sqrt{2}a \times c)$ supercell, with the primitive M point folded to Γ. The band structure is not much perturbed by the stretching of the Fe-As bonds in the paramagnetic state [Fig. 4(b)]. The main effect is the increase in the splitting between the $d_{3z^2-r^2}$ bands that appear at −0.1 and −0.4 eV at Γ in the unperturbed structure. The maximum deformation potential is ~3 eV/Å and it occurs for states

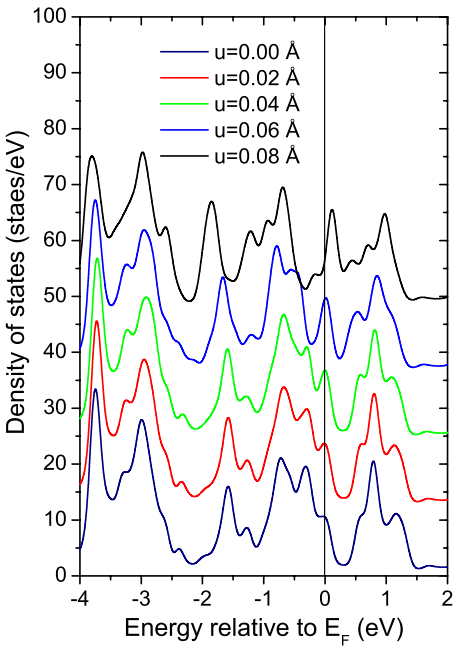

FIG. 5. (Color online) Total densities of states of the antiferromagnetic state, for different vibration displacements u of the A_{1g} phonon at Γ for LaOFeAs, doped with 0.275 electrons/f.u. For clarity, the curves have been shifted and smoothed with a Gaussian broadening of 0.1 eV. Lower to upper curves correspond to increasing values of u.

with almost no weight at the Fermi level E_F, in agreement with Boeri *et al.*[11] The rest of the bands are slightly perturbed by the atomic distortion.

In contrast, the electronic structure is strongly perturbed in both the AF1 and the noncollinear antiferromagnetic states, which remove several band degeneracies [Figs. 4(c) and 4(d)]. In addition, As-mediated antiferromagnetism between Fe atoms opens a pseudogap and therefore removes states from about 0.2 eV below E_F, while a new peak in the density of states appears close to E_F (Fig. 5). This new peak is due to the flattening of the electron pocket bands at the Γ point, right at E_F. The peak size, and its energy shift, increases with u, and it crosses E_F for large u (see Fig. 5). The analysis of the partial density of states reveals that the states associated with this peak are fully spin polarized and entirely localized in the Fe atoms as it is apparent in Fig. 6. The pseudogap at around −0.2 eV appears at the crossing of the unperturbed bands at around the original Γ and M hole and electron pockets, mixed now by the antiferromagnetic coupling. This gap increases with u and with the resulting magnetic moment, and it can be considered as the polaronic level shift introduced by Alexandrov and Mott.[24]

Due to the anisotropic coupling of magnetic moments with phonons, the calculation of the superconducting λ parameter is very difficult and it may require another formulation of the electron-phonon interaction including antiferromagnetic fluctuations. However, in the conventional language of electron-phonon deformation potentials, Figs. 4 and 5 clearly indicate that the presence of antiferromagnetism gives rise to much larger deformation potentials for states right at the Fermi level.

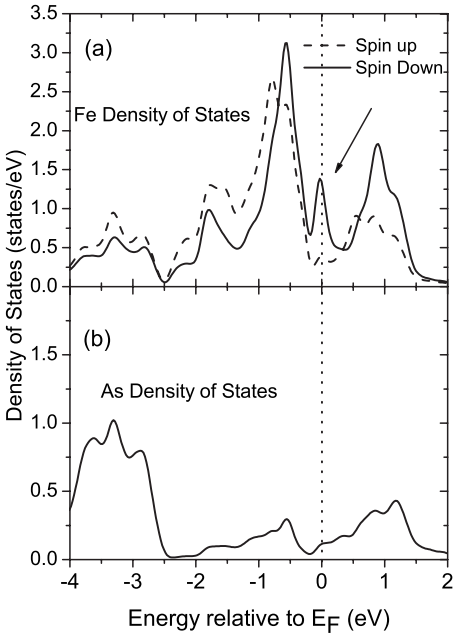

FIG. 6. Spin-resolved local densities of states (LDOSs) for a doping of 0.275 electrons/f.u. and a vibration displacement $u=0.06$ Å of the A_{1g} phonon. (a) LDOS at the Fe atom. (b) LDOS at the As atom. The curves have been smoothed with a Gaussian broadening of 0.1 eV. It can be seen that the density of states peak at the Fermi level (arrow) is fully spin polarized and localized at the Fe atoms.

We therefore suggest a possible general mechanism for BCS-like high-temperature superconductivity in antiferromagnetic compounds with a large on-site electron-electron interaction. It is based on driving them very close to a critical point or line of the antiferromagnetic-to-paramagnetic transition in the pressure-doping phase diagram (we assume here $T=0$). Under these conditions, the lattice distortion of some phonons will switch antiferromagnetism on and off, thus enhancing dramatically their deformation potential and the λ factor.[25]

At this point it is worth mentioning that interplay between a large on-site electron-electron interaction and the electron-phonon interaction has been invoked, using the LDA+U approximation, to explain a large electron-phonon coupling in the half-breathing Cu-O bond stretching mode in cuprate superconductors.[26] Also, the connection between the Fe-As bond length and the magnetic moment in Fe has been discussed by Yildirim.[25]

In our calculations, for computational purposes, we have considered uniform doping. However, in practice chemical doping is inhomogeneous in the nanoscale, which implies that the superconducting band gap will vary spatially or even that patches of normal and superconducting regions will coexist.[27]

V. CONCLUSIONS

In summary, we have shown that the electron-phonon interaction in paramagnetic electron-doped LaOFeAs is more complex and, probably, dramatically larger than previously predicted. The complexity arises from the vicinity of the system to magnetism and, in particular, with the abrupt appearance of phonon-induced magnetic moments at the Fe atoms in an antiferromagnetic As-mediated configuration. The asymmetry of magnetism, with respect to the compression or expansion of the Fe-As bonds, makes the vibrations anharmonic. These results suggest that electron-phonon coupling must be carefully revised, before ruling out its connection with high-temperature superconductivity, in layered compounds close to an antiferromagnetic transition. Calculations of the complex electron-phonon interaction are under way in order to address quantitatively this proposed mechanism.

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[1] Y. Kamihara, H. Hirmatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, J. Am. Chem. Soc. **128**, 10012 (2006).
[2] Y. Kamihara, T. Watanable, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[3] M. R. Norman, Physics **1**, 21 (2008).
[4] Z. Ren, W. Yue-Qin, and Z. Li-Chun, Chin. Phys. Lett. **25**, 2385 (2008).
[5] R. H. Liu *et al.*, Phys. Rev. Lett. **101**, 087001 (2008).
[6] H. Luetkens, H. Klauss, M. Kraken, F. Litterst, T. Dellmann, R. Klingeler, C. Hess, R. Khasanov, A. Amato, C. Baines, J. Hamannborrero, N. Leps, A. Kondrat, G. Behr, J. Werner, and B. Buechner, arXiv:0806.3533 (unpublished).
[7] B. Lorenz, K. Sasmal, R. P. Chaudhury, X. H. Chen, R. H. Liu, T. Wu, and C. W. Chu, Phys. Rev. B **78**, 012505 (2008).
[8] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, Nature (London) **453**, 899 (2008).
[9] V. G. Hadjiev, M. N. Iliev, K. Sasmal, Y.-Y. Sun, and C. W. Chu, Phys. Rev. B **77**, 220505(R) (2008).
[10] S. Raghu, X.-L. Qi, C.-X. Liu, D. J. Scalapino, and S.-C. Zhang, Phys. Rev. B **77**, 220503(R) (2008).
[11] L. Boeri, O. V. Dolgov, and A. A. Golubov, Phys. Rev. Lett. **101**, 026403 (2008).
[12] K. Haule, J. H. Shim, and G. Kotliar, Phys. Rev. Lett. **100**, 226402 (2008).
[13] M. A. Korotin, S. V. Streltsov, A. O. Shorikov, and V. I. Anisi-

mov, J. Exp. Theor. Phys. **107**, 649 (2008).
[14] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[15] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[16] P. Ordejon, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996).
[17] J. Soler, E. Artacho, J. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[18] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
[19] M. Methfessel and A. T. Paxton, Phys. Rev. B **40**, 3616 (1989).
[20] T. Yildirim, Phys. Rev. Lett. **101**, 057010 (2008).
[21] D. J. Singh and M.-H. Du, Phys. Rev. Lett. **100**, 237003 (2008).
[22] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, Nature (London) **453**, 376 (2008).
[23] J. Lorenzana, G. Seibold, C. Ortix, and M. Grilli, Phys. Rev. Lett. **101**, 186402 (2008).
[24] S. Alexandrov and N. F. Mott, Rep. Prog. Phys. **57**, 1197 (1994).
[25] T. Yildirim, Phys. Rev. Lett. **102**, 037003 (2009).
[26] P. Zhang, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **98**, 067005 (2007).
[27] S. H. Pan *et al.*, Nature (London) **413**, 282 (2001).