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Correlated pressure effects on the structure and superconductivity of $LaFeAsO_{0.9}F_{0.1}$

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We have studied the structural and superconducting properties of the compound $LaFeAsO_{0.9}F_{0.1}$ under pressures up to 32 GPa using synchrotron radiation and diamond anvil cells. We obtain an ambient pressure bulk modulus $K_0=78(2)$ GPa compressibility comparable to some cuprates. At high pressures, the sample is in the overdoped region, with a linear decrease with pressure variation of the superconducting transition temperature.

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The discovery of superconductivity[1–4] with critical temperatures between 30 and 55 K in two families of layered iron arsenides has triggered a large amount of work on the subject; as the strong magnetic character of these oxypnictides suggest the possibility of unconventional superconductivity mechanisms. Pressure measurements are of great utility in the study of superconductivity, as is exemplified by the highest measured superconducting[5] transition temperature in fluorinated $HgBa_2Ca_2Cu_3O_{8+\delta}$, $T_c=166$ K at 26 GPa, or the superconductivity in the high ε pressure phase of iron.[6] Coupling the variation under pressure of superconducting properties and the lattice of the studied compound can be a key in the comprehension of the materials and are extremely useful to test with theoretical calculations. The reported measured pressure properties of the $LaFeAsO_{1-x}F_x$ system presents some similarities with the behavior of cuprates (for review see Ref. 7), in particular the passage under pressure from an underdoped to overdoped regime[2] implying a charge transfer under pressure between the LaO and FeAs layers. In order to provide elements for this type of analysis we have performed measurements of the evolution of the structure and of the superconducting properties of similarly prepared samples of $LaFeAsO_{0.9}F_{0.1}$.

Our $LaFeAs(O_{1-x}F_x)$ samples were prepared using high-pressure–high-temperature techniques. The preparation and assembly of the high-pressure cell were performed in a glove box filled with pure argon. Nominal mixtures of FeAs (CERAC 99.5%), La_2O_3, LaF_3 and La or Fe, Fe_2O_3, As, and LaAs (prepared as in Ref. 8) were used. Each mixture was pressed into a pellet and introduced in closed homemade *h*-BN crucibles, which are placed inside tubular carbon furnaces. The whole assembly was put in the high-pressure gasket made of pyrophillite. The setup was pressurized to 3–3.5 GPa in a belt-type apparatus and heated at 1200 °C for a dwell time of 1–4 h, then quenched to room temperature. The conditions were optimized to decrease the proportion of FeAs, LaAs, and LaOF [quickly converted in $La(OH)_3$ in contact with air] impurities and obtain nearly pure phases.

The angle dispersive x-ray diffraction (XRD) studies on $LaFeAsO_{0.9}F_{0.1}$ powder samples were performed at the ID27 high-pressure beamline of the European Synchrotron Radiation Facility using monochromatic radiation ($\lambda=0.3738$ Å) and diamond anvil cells with 350 μm cullet diamonds. Two transmitting media were used: 4:1 methanol-ethanol mixture for the low-pressure range ($P<3$ GPa) and neon for the high-pressure one ($P>3$ GPa). The pressure was determined using the shift of the fluorescence line of the ruby. All the structural studies have been done at ambient temperature. The diffraction patterns were collected with a charge coupled device (CCD) camera, and the intensity vs 2theta patterns were obtained using the FIT2D software.[9] A complete Rietveld refinement was done with the GSAS-EXPGUI package.[10] The electrical resistance measurements were performed using a Keithley 238 source meter and a Keithley 2182 nanovoltmeter. Pressure measurements, 1.4–22 GPa (between 4.2 and 300 K), were done in a sintered diamond Bridgman anvil apparatus using a pyrophillite gasket and two steatite disks as the pressure medium.[11]

In Fig. 1(a) we show the ambient pressure x-ray diffraction pattern and the Rietveld refinement. The lattice parameters are $a=4.004(1)$ Å and $c=8.689(1)$ Å for the $LaFeAsO_{0.9}F_{0.1}$ sample used in the high-pressure XRD experiment. Compared to the values for pure LaFeAsO (Ref. 12) and fluorine doped samples from the literature,[1] our sample state corresponds to an overdoped sample. Unfortunately, by x-ray diffraction, it is not possible to determine the real fluorine content of the sample by Rietveld refinement. Nevertheless, the occupancy factor of the (O,F) site was estimated to be nearly full and probably the fluorine content is near the nominal composition, i.e., $x=0.1$, because the

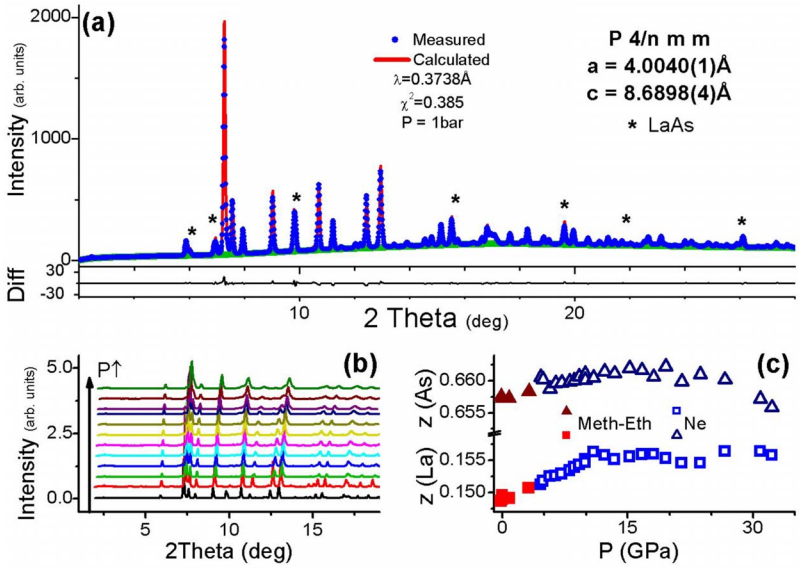

FIG. 1. (Color online) (a) X-ray synchrotron radiation diffraction pattern of the $LaFeAsO_{0.9}F_{0.1}$ powder sample at ambient pressure. The Rietveld refinement is the red solid line. The black stars represent the LaAs impurity phase. (b) Pressure evolution of the diffraction patterns of $LaFeAsO_{0.9}F_{0.1}$. The solid arrow indicates the increasing pressure sense. The data correspond to 0, 3.2, 4.6, 5.7, 7.1, 8.6, 9.9, 12.2, 15.2, 18.1, 21.5, and 30.9 GPa, respectively. (c) Pressure dependence of the z atomic position of the La and As atoms. Solid symbols correspond to methanol-ethanol pressure media, while open symbols correspond to Neon media.

HP-HT treatment is made under hermetic conditions and the loss of fluorine should be negligible.

The pressure evolution of the x-ray diffraction patterns can be seen in Fig. 1(b). No structural transition is observed up to the highest measured pressure, 32 GPa. From the Rietveld refinements, we obtain the pressure dependence of the z atomic position of La and As [see Fig. 1(c)] that shows a weak increment in the range $P<10$ GPa and then a saturation with no signature of a phase transition.

The unit-cell volume, V, at various pressures P were fitted to a third-order Murnaghan equation of state $V=V_0(1+K_0'P/K_0)^{-1/K_0}$, where K_0 is the bulk modulus at ambient conditions and $K_0'=7.4(2)$. We obtain a value for the bulk modulus of 78(2) GPa that is very similar to those found in cuprates[13] but slightly lower than the 98 GPa obtained from theoretical calculations.[14] In Table I we show the values of the lattice parameters of $LaFeAsO_{0.9}F_{0.1}$ for the different measured pressures.

It is interesting to note that all the superconducting compounds with the highest T_c (cuprates, MgB_2, and oxypnictides) are of layered structure. As such, it is important to determine how pressure changes the interaction between the layers, interaction that can be measured by the relative compression of the c parameter with respect to the a parameter. We observe in Fig. 2(b) that it is more important in the shown cuprate and in the $Na_{0.5}CoO_2$ cobaltite than in $LaFeAsO_{0.9}F_{0.1}$, implying a less two-dimensional character in the oxypnictides, at least in what considers lattice properties.

In Fig. 3 we show the evolution of the temperature dependence of resistance of $LaFeAsO_{0.9}F_{0.1}$ as a function of pressure. The absolute value decreases with compression, as well as the resistance slope α. The resistivity of a metal can be written as[15]

$$R=\frac{12\pi^3\hbar}{e^2\int_{FS}\Lambda_k dS_F}\approx\frac{12\pi^3\hbar}{e^2\Lambda}\frac{1}{\int_{FS}dS_F},$$

where e is the electronic charge and Λ_k the mean free path for each vector k on the Fermi surface (FS). If we approximate $\Lambda_k\approx\Lambda$, constant on all the FS, the inverse of the resistance slope, α^{-1}, is directly proportional to the area of the FS. We observe that this parameter increases linearly with pressure, Fig. 3 inset, that can be interpreted in a first approximation as a constant charge transfer dn/dP with pres-

TABLE I. Refined lattice parameters as a function of applied pressure. The error in pressure determination is estimated to 0.05 GPa.

Pressure (GPa)	a (Å)	c (Å)	Volume (Å^3)
0.00	4.0040(1)	8.6898(4)	139.31(1)
0.82	3.9986(1)	8.6410(3)	138.16(1)
3.16	3.9705(1)	8.5477(3)	134.75(1)
4.58	3.9529(2)	8.4678(7)	132.32(1)
4.85	3.9514(2)	8.4574(6)	132.05(1)
5.68	3.9443(2)	8.4325(6)	131.19(1)
6.36	3.9387(2)	8.4137(7)	130.52(1)
7.08	3.9329(2)	8.3930(6)	129.82(1)
8.06	3.9251(2)	8.3646(7)	128.87(1)
8.60	3.9216(2)	8.3476(8)	128.38(1)
9.19	3.9184(2)	8.3327(8)	127.94(1)
9.90	3.9143(3)	8.3116(9)	127.35(1)
10.91	3.9085(3)	8.2834(9)	126.54(1)
12.22	3.9012(3)	8.2549(10)	125.62(1)
13.41	3.8956(3)	8.2247(10)	124.82(1)
15.22	3.8869(3)	8.1833(11)	123.64(2)
16.70	3.8793(4)	8.1513(12)	122.67(2)
18.10	3.8733(4)	8.1214(13)	121.84(2)
19.56	3.8671(4)	8.0913(14)	121.00(2)
21.46	3.8603(5)	8.0513(15)	119.98(2)
23.69	3.8519(5)	8.0089(16)	118.83(3)
26.63	3.8436(6)	7.9493(19)	117.43(3)
30.87	3.8345(7)	7.8494(25)	115.41(3)
32.26	3.8310(8)	7.8330(30)	114.96(4)

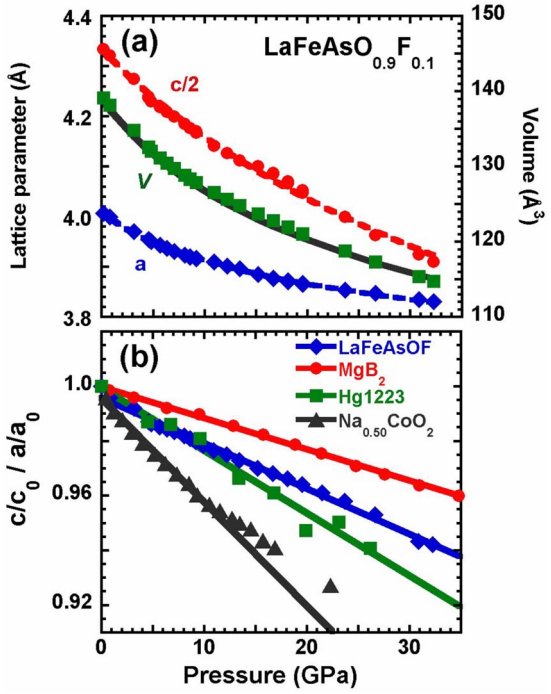

FIG. 2. (Color online) (a) Evolution of the lattice parameters as a function of pressure. Blue diamonds: a, red dots: $c/2$, and green squares: volume. The solid black line corresponds to Murnaghan equation of state (see text). (b) Comparison of the ratio of the basal parameter to the ratio of the stacking parameter for different high-temperature superconductors. Blue diamonds: $LaFeAsO_{0.9}F_{0.1}$ (this Rapid Communication), red dots: MgB_2 (Ref. 19), green squares: Hg–1223 (Ref. 13), and black up triangles: $Na_{0.5}OCo_2$ (Ref. 20).

sure, as has been used to describe the behavior of cuprates under pressure.[7] Hall constant measurements under pressure would be necessary to confirm this assumption.

In Fig. 4(a) we show the variation of the superconducting transition temperature of our sample compared to the one reported by Takahashi *et al.*[2] T_c onset is defined as in Ref. 2, while $T_c$mid is obtained from the peak in the derivative of the resistance. The comparison suggests that our sample is more on the overdoped region than the one measured by

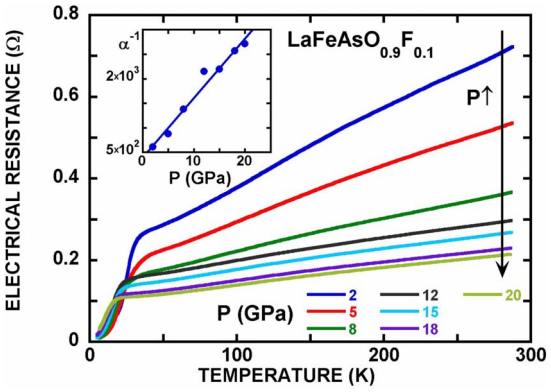

FIG. 3. (Color online) Electrical resistance of $LaFeAsO_{0.9}F_{0.1}$ sample as a function of temperature for different pressures a indicated in the figure. Resistance decreases monotonously with pressure.

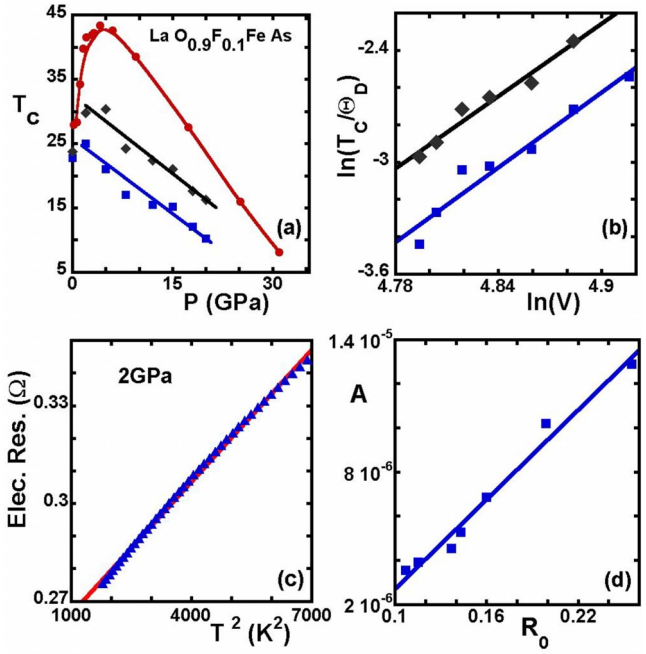

FIG. 4. (Color online) (a) Superconducting T_cs as a function of pressure: red dots Takahashi *et al.* (Ref. 2) onset data; black diamonds: our onset data; blue squares: our midtransition data. (b) Dependence of the logarithmic ratio of T_c with the logarithm of the volume as a function of pressure. (c) Electrical resistance of the sample at 2 GPa as a function of the square of the temperature showing the $R=R_0+AT^2$ law. (d) Linear dependence of A with R_0. The value of the slope, 6×10^{-5}, implies that the quadratic dependence is due to the Koshino-Taylor mechanism, inelastic scattering against impurities.

Takahashi *et al.* although the nominal composition is similar. It should be noted that the samples used for pressure measurements are extremely small and that weak nonhomogeneities in the bulk sample can result in having a measured sample that is not of the nominal composition. In any way, we observe a linear variation of T_c that would imply if we accept the constant charge transfer that the dependence of T_c with carrier concentration is not strictly parabolic as in cuprates or that other factors come into play. According to Levy and Olsen,[16] within conventional electron-phonon coupling BCS theory the logarithmic volume dependence of T_c follows

$$\frac{d\ln(T_c/\Theta_D)}{d\ln V} = \ln\left(\frac{\Theta_D}{T_c}\right)\frac{d\ln(\lambda)}{d\ln V} \equiv \ln\left(\frac{\Theta_D}{T_c}\right)\varphi,$$

where Θ_D is the Debye temperature, λ the electron-phonon coupling parameter, and $\varphi\approx2.5$ for conventional superconductors. From our results on our variation of T_c and volume with pressure on $LaFeAsO_{0.9}F_{0.1}$ and using[17] a $\Theta_D=316$ K, we obtain a $d\ln(T_c/\Theta_D)/d\ln V=6.5$, both for the onset and the middle of the transition [see Fig. 4(b)]. We obtain then $\varphi\approx2.75$, compatible with electron-phonon coupling, although, on one hand, Levy and Olsen's semiempirical analysis is valid at low pressures (<1 GPa) and must be correlated with a hypothetic isotope effect to be conclusive. On

the other hand we have ignored any variation of Θ_D with pressure as no such measurement is available.

As we are seemingly in an overdoped sample, we can look for Fermi-liquid behavior as has been observed in cuprates, i.e., in electrical resistance a quadratic term in temperature due to Landau quasiparticle-quasiparticle scattering (LQQS). The resistance above the superconducting transition follows approximately a law AT^n, with $n \approx 2$ [see Fig. 4(c)]. However, we must strongly remark that this is not the signature of LQQS, as A follows a linear law with the residual resistance R_0 as pressure is changed with a coefficient of 6×10^{-5}, Fig. 4(d), indicating conclusively that carrier scattering preceding the superconducting transition in the sample is dominated by inelastic scattering against defects and impurities, the Koshino-Taylor mechanism.[18]

Samples with less defects and impurities will be needed to determine if the overdoped region is dominated by Fermi-liquid quasiparticle-quasiparticle scattering as in cuprates. In conclusion, we have measured the structural and transport properties of $LaFeAsO_{0.9}F_{0.1}$ under pressure. We find no evidence of a phase transition up to 32 GPa, a compressibility similar to that of cuprates and an apparent constant charge transfer under pressure. The correlated variation under pressure of T_c and volume is compatible with conventional superconductivity. The quadratic temperature dependence of the resistivity is not due to Landau quasiparticle-quasiparticle scattering as in overdoped cuprates but to quasiparticle inelastic scattering against impurities.

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