

# Intrinsic dependence of $T_c$ on hydrostatic (He-gas) pressure for superconducting LaFePO, PrFePO, and NdFePO single crystals

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Since their discovery in 2008, the Fe-based superconductors have attracted a great deal of interest. Regrettably, the mechanism(s) responsible for the superconductivity has yet to be unequivocally identified. High pressure is an important variable since its application moderates the pairing interaction. Thus far, the  $LnFePO$  ( $Ln = La, Pr, Nd, Sm, Gd$ ) family of superconductors has received relatively little attention. Early high-pressure studies on LaFePO found that  $T_c$  initially increased with pressure before passing through a maximum at higher pressures. The present studies on both polycrystalline and single-crystalline LaFePO, PrFePO, and NdFePO utilize the most hydrostatic pressure medium available, i.e., dense He. Surprisingly, for all samples,  $T_c$  is found to initially *decrease* rapidly with pressure at the rate  $dT_c/dP \simeq -2$  to  $-3$  K/GPa. Less hydrostatic pressure media thus appear to enhance the value of  $T_c$  in these materials. These results give yet further evidence that the superconducting state in Fe-based superconductors is extraordinarily sensitive to lattice strain.

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## I. INTRODUCTION

The discovery in 2008 of superconductivity at  $T_c = 26$  K in  $LaFeAsO_{1-x}F_x$  (Ref. 1) spurred a flurry of research on the Fe-based superconductors. Among these materials, the rare-earth transition-metal phosphide oxides  $LnFePO$  ( $Ln = La, Pr, Nd, Sm, Gd$ ) have not been studied as extensively due to their lower superconducting temperatures. These compounds were first synthesized in 1995 and found to crystallize in a tetragonal  $ZrCuSiAs$ -type structure.<sup>2</sup> A decade later, Kamihara *et al.*<sup>3</sup> discovered superconductivity in LaFePO near 4 K followed by superconductivity at comparable temperatures in SmFePO,<sup>4</sup> PrFePO and NdFePO,<sup>5</sup> and GdFePO,<sup>6</sup> CeFePO remained nonsuperconducting to 400 mK.<sup>7</sup> Like other Fe-based superconductors, these compounds consist of alternating layers of lanthanide oxide ( $Ln^{3+}O^{2-}$ ) and iron pnictide ( $Fe^{2+}P^{3-}$ ).<sup>1-3</sup>

As is found for the superconducting cuprates, the “parent” compound for the Fe-based pnictides exhibits an antiferromagnetic phase which is suppressed through either doping or high pressure, leading to a superconducting phase where  $T_c$  initially increases and passes through a dome-shaped curve before disappearing.<sup>8</sup> High pressure has proven to be a valuable technique in the field of superconductivity where it can be used to help synthesize new superconductors as well as to give hints on how to increase  $T_c$  through lattice pressure. However, perhaps the most important potential application of high pressure is its use as a quantitative tool to further our understanding of the superconducting state itself, a state which is believed to be unconventional in both the pnictides and cuprates. An example for the use of high pressure as a quantitative tool is the combined uniaxial and hydrostatic (He-gas) high-pressure studies on optimally doped cuprate single crystals where it was found that the superconducting state is strengthened either by compressing the  $CuO_2$  planes or by pulling them further apart.<sup>9</sup> A similar

result was recently observed for the optimally doped pnictide  $LaFeAsO_{1-x}F_x$ .<sup>10,11</sup>

Early high-pressure measurements on the underdoped pnictide superconductor LaFePO agreed that the transition temperature  $T_c$  initially increases under pressure before passing through a maximum.<sup>12,13</sup> However, the detailed dependencies  $T_c(P)$  observed were otherwise very different. In an experiment carried out in a gasketed diamond-anvil cell without pressure medium, the LaFePO crystal was crushed between opposing diamond anvils as pressure was applied.  $T_c$  was found to initially increase at the rate  $dT_c/dP = +0.5$  K/GPa,  $T_c(P)$  passing through a maximum at  $P_{max} = 5.4$  GPa.<sup>12</sup> On the other hand, as seen in Fig. 1, electrical resistivity measurements on polycrystalline LaFePO in a piston-cylinder pressure cell to 1.5 GPa using Fluorinert FC-70/77 pressure medium showed a much steeper initial pressure increase  $dT_c/dP = +4$  K/GPa,  $T_c(P)$  passing through a maximum near 1 GPa.<sup>13</sup> The marked change in the high-pressure environment thus appears to strongly affect the pressure dependence  $T_c(P)$ , the shear stresses exerted on the LaFePO sample in the diamond-anvil cell being much larger than those in the experiment with Fluorinert pressure medium.

The sensitivity of the magnetic, structural, and superconducting properties of the Fe-based systems to shear stress has been pointed out in several reviews.<sup>8,14</sup> In fact, a number of authors conclude from their experiments on these materials that a higher degree of lattice strain actually strengthens superconductivity, if it is present, or favors its appearance, if it is not.<sup>15-19</sup> To establish the “intrinsic”  $T_c(P)$  dependence for LaFePO, the most hydrostatic pressure medium available, dense He, was chosen for the present experiments on LaFePO, PrFePO, and NdFePO single crystals. For all three, we find, in fact, that under hydrostatic pressures to 0.8 GPa,  $T_c$  decreases rapidly with pressure. These results emphasize the care which must be taken to extract the intrinsic dependence of  $T_c$  on pressure for the Fe-based pnictides.

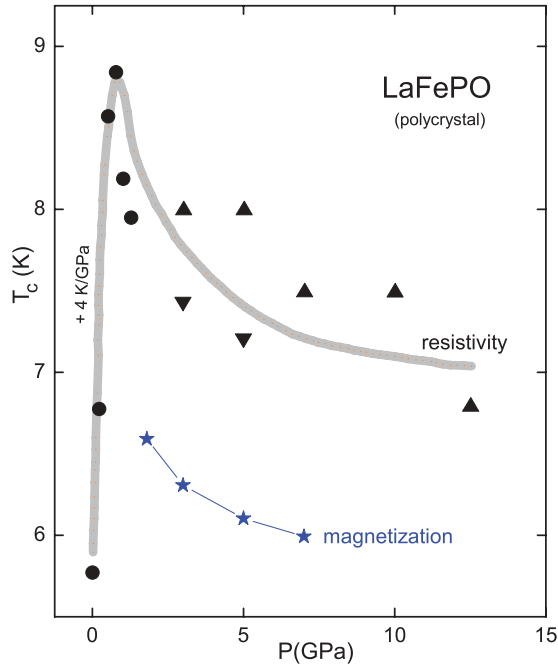


FIG. 1. (Color online) Dependence of the superconducting transition temperature  $T_c(P)$  on pressure for polycrystalline LaFePO from Ref. 13 determined by measurements of the electrical resistivity (●: piston-cylinder cell with Fluorinert FC-70/77; ▲, ▼: DAC with NaCl) and the dc magnetization (★: DAC with methanol-ethanol). After a rapid initial rise,  $T_c(P)$  is seen to peak at  $\sim 1$  GPa. Wide gray line is a guide to the eye.

## II. EXPERIMENTAL DETAILS

### A. Sample preparation

Single crystals of LaFePO, PrFePO, and NdFePO were grown from elements and elemental oxides with purities  $>99.9\%$  in molten Sn:P flux. The growth took place over a one-week period in quartz ampoules sealed with 75-torr Ar at room temperature. The inner surface of each quartz ampoule was coated with carbon by a pyrolysis method. The starting materials were La,  $\text{Fe}_2\text{O}_3$ , P, and Sn, which were combined in the molar ratios 9:3:6:80.5, similar to previous reports for P-based oxypnictide single crystals.<sup>5,12,20</sup> The  $\text{Fe}_2\text{O}_3$  powder was dried for  $\sim 10$  h at  $300^\circ\text{C}$  before weighing. The ampoule was heated to  $1135^\circ\text{C}$  at a rate of  $35^\circ\text{C h}^{-1}$ , kept at this temperature for 96 h, and then rapidly cooled to  $700^\circ\text{C}$ . After removing the majority of the flux by spinning the ampoules in a centrifuge, LaFePO, PrFePO, and NdFePO single-crystal platelets of an isometric form, with typical dimensions  $\sim 0.5 \times 0.5 \times 0.05 \text{ mm}^3$  or smaller (particularly for the NdFePO crystals), were collected and cleaned in hydrochloric acid to remove the flux from the surface of the crystals prior to measurements. As previously reported,<sup>5,12</sup> the platelets cleaved easily in the  $ab$  plane and were notably malleable, in contrast to the cuprate superconductors.  $\text{O}_2$ -annealed crystals were heated to  $700^\circ\text{C}$  for 24 h under flowing  $\text{O}_2$ . Henceforth, these samples will be referred to simply as “annealed.” For the ac susceptibility measurements, the masses of the annealed single crystals studied here are LaFePO (1 crystal,  $23 \mu\text{g}$ ), PrFePO (7 crystals,  $75 \mu\text{g}$  total), NdFePO (5 crystals,  $18 \mu\text{g}$

total); an unannealed LaFePO crystal was also measured (1 crystal,  $87 \mu\text{g}$ ).

X-ray powder diffraction measurements were carried out using a Bruker D8 diffractometer and a nonmonochromated Cu  $K\alpha$  source to check the purity and crystal structure of the LaFePO and PrFePO crystals. Due to a small batch yield, diffraction measurements were not attempted for the NdFePO crystals. As reported previously,<sup>12</sup> the malleability of the crystals made it difficult to grind them into a fine powder. The powder diffraction pattern was generated from a collection of single crystals cut into small pieces using a razor blade and then ground into a coarse powder using a mortar and pestle. The diffraction patterns obtained were consistent with those previously reported.<sup>2</sup> Chemical analysis measurements made using an FEI Company Model 600 scanning electron microscope reveal that the stoichiometry for all crystals is consistent with the ratio 1:1:1:1 for  $\text{Ln:Fe:P:O}$ .

Polycrystalline pellets of LaFePO were prepared using the method reported by Kamihara *et al.*<sup>3</sup> The samples were subsequently annealed at  $700^\circ\text{C}$  in flowing Ar for 24 h. The dimensions of the sample studied in resistivity measurements are  $\sim 1.8 \times 4.4 \times 0.67 \text{ mm}^3$ .

### B. Measurement techniques

To generate hydrostatic pressures to  $\sim 1$  GPa, a He-gas compressor (Harwood Engineering) is connected via a long, flexible capillary to a CuBe pressure cell (Unipress, Warsaw) located in a Janis Supravertemp bath cryostat capable of reaching temperatures to 1.5 K. The value of the pressure given in the measurement of  $T_c$  is determined at a temperature near that of the superconducting transition using a calibrated digital manganin gauge located at room temperature in the compressor system. Further details of the He-gas techniques used are given elsewhere.<sup>21</sup>

Measurements of the ac susceptibility were carried out in the He-gas system at 0.1 Oe rms and 1023 Hz by surrounding the sample with a calibrated primary/secondary coil system connected to a Stanford Research SR830 digital lock-in amplifier via an SR554 transformer preamplifier. A temperature-dependent background signal, using a measurement from a previous experiment without sample, was subtracted from the data with sample. The four-point electrical resistivity was measured on LaFePO in both polycrystalline (dc measurement) and single-crystalline (ac measurement in  $ab$  plane at 15 Hz) forms with an excitation current of 1–2 mA. All measurements of  $T_c$  were repeated at least once to verify reproducibility to within 20 mK. Due to appreciable uncertainties in the sample dimensions and geometry of the electrical contacts, the error in the absolute value of the electrical resistivity was  $\pm 20\%$  for polycrystalline and  $\pm 35\%$  for single-crystalline LaFePO.

Less hydrostatic high-pressure ac magnetic susceptibility measurements were performed using a piston-cylinder cell containing a Teflon capsule filled with Fluorinert FC-70 as pressure medium. FC-70 is known to remain hydrostatic at ambient temperature only to  $\sim 0.55$  GPa.<sup>22</sup> The magnitude of the transition in the ac susceptibility was consistent with full shielding. Pressure was adjusted at room temperature and measured at low temperature using the superconducting

transition of a small piece of tin<sup>23</sup> located near the LaFePO crystal.

Measurements to much higher pressures were carried out in a diamond-anvil pressure cell (DAC) with two opposing  $\frac{1}{6}$ -carat, type-Ia diamonds. The pressure was determined *in situ* by placing small ruby spheres<sup>24</sup> in the sample space. The given values of the pressure were determined at 5–10 K with a resolution of  $\pm 0.2$  GPa using the revised ruby pressure scale of Chijioke *et al.*<sup>25</sup> For experiments under hydrostatic pressure conditions, He was used as a pressure medium since it remains fluid to a higher pressure and lower temperature than any other substance. Even when He solidifies, it is a relatively soft solid and can only exert weak shear stresses on the sample it surrounds. This, therefore, makes He the ideal pressure medium for hydrostatic pressure studies. A single crystal sample was placed in a 260- $\mu\text{m}$ -diameter hole electrosark drilled through the center of a gold-plated CuBe gasket (3 mm in diameter, 260  $\mu\text{m}$  thick), preindented to a thickness of 50  $\mu\text{m}$  by two diamond anvils with 0.5-mm-diameter culets. For nonhydrostatic pressure measurements, no pressure medium was used so that the opposing diamond anvils pressed directly onto the sample. Here, two diamond anvils with 0.9-mm culets were used together with a CuBe gasket (3 mm diameter, 400  $\mu\text{m}$  thick) preindented to 150  $\mu\text{m}$ .

The DAC was placed in a continuous-flow cryostat (Oxford Instruments) and submerged in liquid He. After some initial pressure was applied, temperatures were kept below 65 K throughout the experiment. The ac susceptibility measurements were carried out at 1023 Hz using a 3 Oe or 0.1 Oe rms primary field for the hydrostatic or nonhydrostatic measurements, respectively. The transition was detected using a balanced primary/secondary coil system similar to that above for the He-gas system. Further experimental details on the DAC techniques used may be found elsewhere.<sup>26–28</sup>

### III. RESULTS OF EXPERIMENT

In view of the differing  $T_c(P)$  dependencies obtained previously under varying pressure environments,<sup>12,13</sup> it was advisable to determine the *intrinsic* pressure dependence  $T_c(P)$  for single-crystalline samples by subjecting them to purely hydrostatic He-gas pressure. In Fig. 2, the real part of the ac susceptibility of LaFePO, PrFePO, and NdFePO single crystals is plotted versus temperature at several pressures. Following the determination of  $T_c$  at ambient pressure (0 GPa), a pressure near 0.9 GPa was applied at room temperature before cooling down to measure  $T_c$ . In subsequent measurements, the pressure was reduced at low temperature (40–80 K) and  $T_c$  remeasured. Within experimental error, the value of  $T_c$  upon full pressure release returned to its initial value. Surprisingly, for all three crystals it is seen in Fig. 2 that  $T_c$  decreases rapidly with pressure, in contrast to the positive initial pressure dependence reported earlier for LaFePO from resistivity measurements.<sup>12,13</sup>

To check the unlikely scenario that this differing sign of  $dT_c/dP$  might depend on the measurement technique (resistivity versus ac susceptibility) or on whether the sample is polycrystalline or single-crystalline, electrical resistivity measurements were carried out under He-gas pressure on both

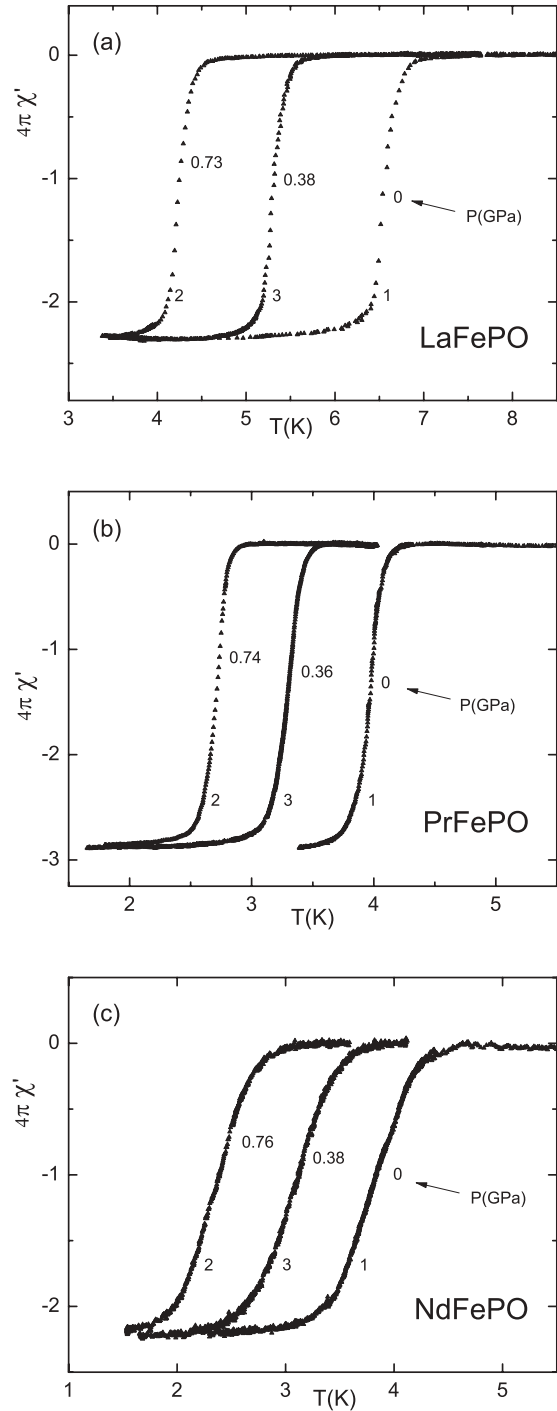


FIG. 2. Real part of the ac susceptibility versus temperature at several hydrostatic (He-gas) pressures for (a) an unannealed LaFePO crystal, (b) an annealed PrFePO crystal, and (c) an annealed NdFePO crystal. Numbers give order of measurement. No correction for the demagnetization factor is made.  $T_c$  is determined from the transition midpoint and clearly decreases as pressure is applied.

polycrystalline and single-crystalline LaFePO (see Fig. 3). Here also,  $T_c$  is seen to decrease rapidly under pressure.

In Fig. 4, the results of all ac susceptibility and electrical resistivity measurements on annealed and unannealed LaFePO crystals and the polycrystal are shown. In all measurements,  $T_c$  is seen to decrease rapidly with pressure; the values of

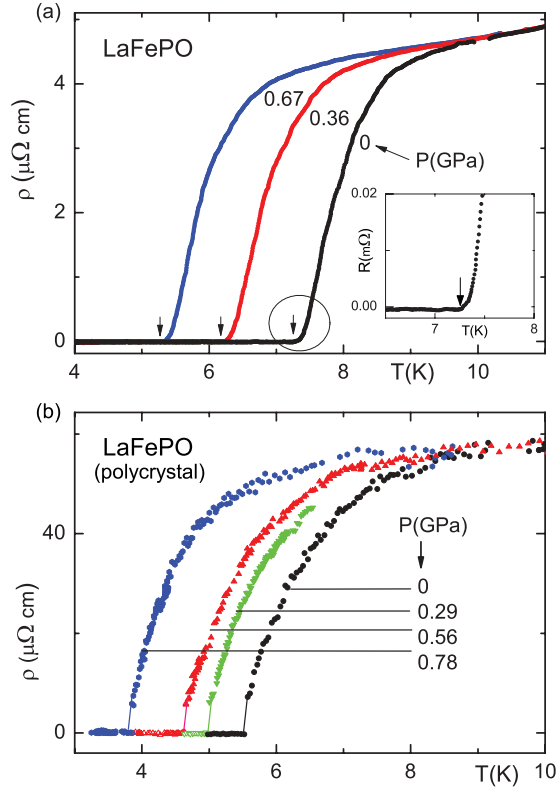


FIG. 3. (Color online) Electrical resistivity versus temperature at several hydrostatic (He-gas) pressures for (a) *ab* plane of an annealed LaFePO single crystal and (b) an unannealed LaFePO polycrystal. Vertical arrows give values of  $T_c$  as determined from the temperature where the resistivity disappears (see inset).  $T_c$  clearly decreases as pressure is applied.

$dT_c/dP$  obtained are listed in the inset. The rate of change of  $T_c$  with hydrostatic pressure is seen to not depend sensitively on the property measured or whether the LaFePO sample is polycrystalline, single-crystalline, annealed, or unannealed.

Very similar results were obtained for annealed single crystals of PrFePO and NdFePO; the values of  $|dT_c/dP|$  are less by  $\sim 30\%$  compared to those of LaFePO; this is consistent with the fact that the values of  $T_c$  at ambient pressure are also less by approximately the same amount. Due to the relatively small size of the PrFePO and NdFePO crystals (for details, see Sec. II A), several crystals were measured together to enhance the signal-to-noise ratio in the ac susceptibility measurement.

In earlier hydrostatic ac susceptibility measurements on a single crystal of annealed PrFePO in a DAC, we found  $T_c \simeq 4.4$  K at ambient pressure. Upon application of an initial pressure of 1.8 GPa in the DAC with He pressure medium, no transition could be observed above 1.4 K. This is consistent with the results of the present He-gas studies where, from Fig. 4,  $dT_c/dP \simeq -1.70(7)$  K/GPa. At 1.8 GPa, the transition onset would have dropped to  $\sim 1.3$  K, which is just below the accessible temperature range in the present experiment.

The negative pressure dependence of  $T_c$  seen in all measurements in Fig. 4 stands in stark contrast to the positive dependence reported in the two earlier studies.<sup>12,13</sup> This difference likely originates from the high hydrostaticity of the He-gas pressure medium in the present experiments. In a

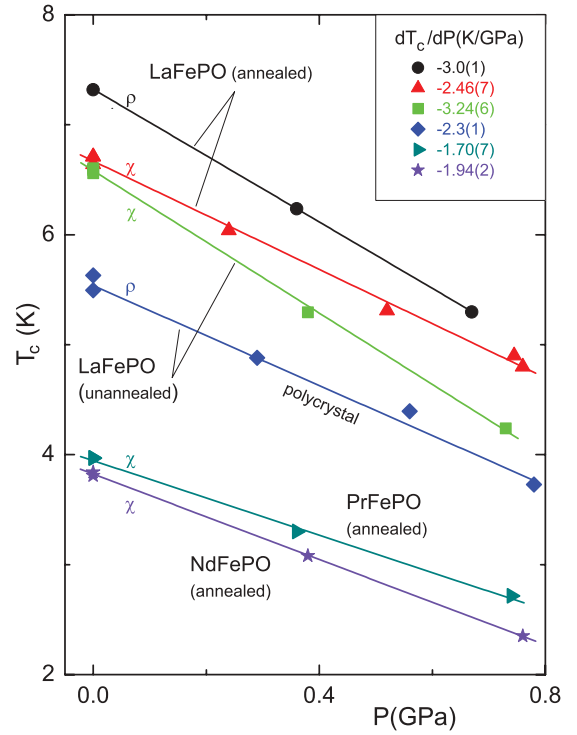


FIG. 4. (Color online) Summary graph giving dependence of  $T_c$  on hydrostatic He-gas pressure for all samples studied. The legend gives values of pressure derivative  $dT_c/dP$ ; straight lines are guides to the eye. For all samples,  $T_c$  decreases rapidly with pressure to 0.8 GPa.

bid to reproduce the pressure conditions in the Igawa *et al.*<sup>13</sup> measurement, a piston-cylinder ac susceptibility experiment was carried out on a single-crystalline LaFePO sample using Fluorinert FC-70 pressure medium. Several measurements were taken upon increasing the pressure up to  $\sim 1.1$  GPa (see Fig. 5). The pressure was then increased above 2 GPa,

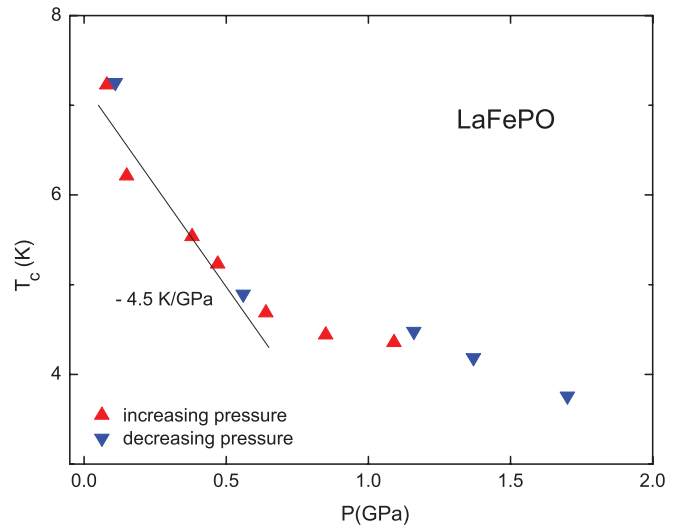


FIG. 5. (Color online) Dependence of  $T_c$  for a LaFePO crystal on pressure generated in a piston-cylinder cell with Fluorinert FC-70 pressure medium.  $T_c$  is seen to decrease monotonically with pressure to 1.7 GPa. Straight line is a guide to the eye.



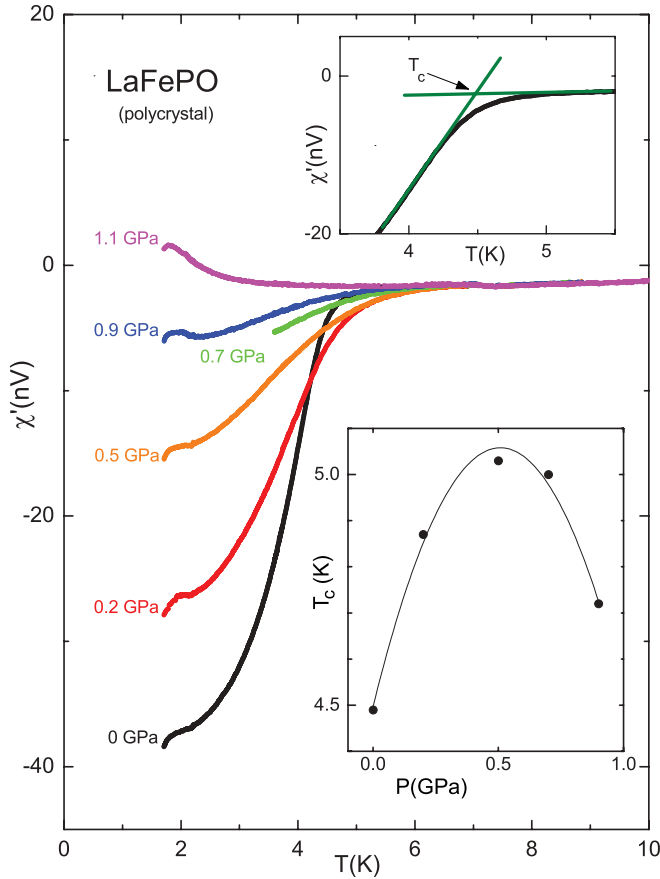


FIG. 6. (Color online) Real part of the ac susceptibility signal (in nanovolts) versus temperature for an unannealed polycrystalline LaFePO sample using a diamond-anvil cell without pressure medium.  $T_c$  clearly increases initially as pressure is applied. A background subtraction (assumed to be pressure independent) was made. The magnitude of the superconducting transition decreases rapidly with increasing pressure. Here,  $T_c$  is determined from the superconducting onset as seen in the upper inset. The lower inset shows that  $T_c$  increases initially with pressure but passes through a maximum near 0.5 GPa. Curved line is a guide to the eye.

but the superconducting transition of LaFePO could not be clearly resolved, presumably due to a partial overlap with the superconducting transition of the Sn manometer. Several additional measurements were then taken during unloading. Surprisingly, as seen in Fig. 5,  $T_c$  initially decreases rapidly under pressure.

Finally, in an effort to reproduce the nonhydrostatic high-pressure DAC measurements of Hamlin *et al.*<sup>12</sup> an unannealed, polycrystalline LaFePO sample was loaded into the gasket hole without adding any pressure medium. The sample was then crushed between the opposing diamond anvils as pressure was applied. At ambient pressure, the ac susceptibility measurement in Fig. 6 shows a broad superconducting transition. As the pressure is increased, the size of the transition is seen to decrease, most likely due to the sample being broken up into smaller pieces as it was crushed between the anvils.  $T_c$  is seen in the lower inset to Fig. 6 to initially increase with pressure but pass through a maximum at  $\sim 0.5$  GPa, a pressure well below that at  $\sim 5.4$  GPa observed in the experiment of Hamlin

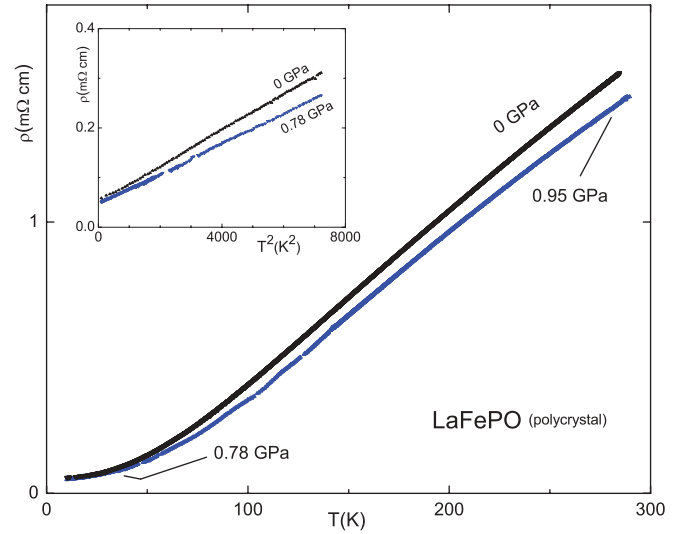


FIG. 7. (Color online) Electrical resistivity for an unannealed LaFePO polycrystal at ambient pressure (black data) and at high pressure (blue data) over the temperature range 1.5 to 300 K. Upon cooling, pressure decreased from 0.95 GPa at room temperature to 0.78 GPa at low temperature. The inset shows that below 85 K, the resistivity is proportional to  $T^2$ . At a given temperature, the resistivity always decreases under pressure.

*et al.*<sup>12</sup> The important point is that a positive initial pressure derivative  $dT_c/dP$  is obtained in this strongly nonhydrostatic measurement on LaFePO.

The electrical resistivity of polycrystalline LaFePO was measured at both ambient and high He-gas pressure as a function of temperature over the range 1.5–300 K (see Fig. 7). Note that the pressure applied at ambient temperature (0.95 GPa) reduces to 0.78 GPa at temperatures near  $T_c$ . In the inset to Fig. 7, the resistivity is plotted versus  $T^2$  to 85 K and is seen at both pressures to follow the dependence  $\rho = \rho_o + AT^2$ , yielding at ambient pressure  $\rho_o = 505 \times 10^{-4}$  mΩ cm,  $A = +362 \times 10^{-7}$  mΩ cm and at high pressure  $\rho_o = 466 \times 10^{-4}$  mΩ cm,  $A = +302 \times 10^{-7}$  mΩ cm. Both  $\rho_o$  and  $A$  thus decrease with pressure. At temperatures above 100 K, the temperature-dependent resistivity exhibits a mild negative curvature. Holding the values of  $\rho_o$  and  $A$  fixed, the resistivity data in Fig. 7 are well fit ( $R^2 \simeq 0.999$ ) over the entire temperature range 1.5–300 K by the expressions

$$\begin{aligned} \rho(0 \text{ GPa}) = & (505 \times 10^{-4}) + (362 \times 10^{-7})T^2 \\ & - (122 \times 10^{-9})T^3 + (572 \times 10^{-11})T^4 \\ & - (90.9 \times 10^{-12})T^5 + (639 \times 10^{-15})T^6 \\ & - (235 \times 10^{-17})T^7 + (445 \times 10^{-20})T^8 \\ & - (342 \times 10^{-23})T^9 \text{ mΩ cm} \end{aligned}$$

and

$$\begin{aligned} \rho(0.95 \text{ GPa}) = & (466 \times 10^{-4}) + (302 \times 10^{-7})T^2 \\ & - (99.4 \times 10^{-9})T^3 + (329 \times 10^{-11})T^4 \\ & - (35.6 \times 10^{-12})T^5 + (145 \times 10^{-15})T^6 \\ & - (16.9 \times 10^{-17})T^7 + (32.4 \times 10^{-20})T^8 \\ & - (71.8 \times 10^{-23})T^9 \text{ mΩ cm.} \end{aligned}$$

From the values of the resistivity at 300 K,  $\rho(0 \text{ GPa}) = 1630 \mu\Omega \text{ cm}$  and  $\rho(0.95 \text{ GPa}) = 1530 \mu\Omega \text{ cm}$ , the residual resistivity ratios take on the values  $\text{RRR} = \rho_{300 \text{ K}}/\rho_0 = 32$  and 33, respectively. The residual resistivity ratio (RRR) for this polycrystalline sample is the same as the value 32 reported earlier from resistivity measurements in the  $ab$  plane of a LaFePO single crystal originating from the same group.<sup>5</sup> However, the coefficient of  $T^2$  in this earlier measurement  $A = 0.00946 \mu\Omega \text{ cm K}^{-2}$  differs appreciably from the present value  $0.0362 \mu\Omega \text{ cm K}^{-2}$  at ambient pressure. This difference is almost certainly due to the fact that the present resistivity measurements are on polycrystalline LaFePO, whereas the earlier studies<sup>5</sup> measured the resistivity in the  $ab$  plane of a single crystal. The present ambient-pressure value of the resistivity at 300 K,  $1630 \mu\Omega \text{ cm}$ , agrees reasonably well, within our large ( $\pm 20\%$ ) experimental error, with published values on polycrystalline LaFePO, namely,  $1510 \mu\Omega \text{ cm}$ ,<sup>29</sup>  $2100 \mu\Omega \text{ cm}$ ,<sup>30</sup> and  $2500 \mu\Omega \text{ cm}$ .<sup>31</sup> The resistivity of a polycrystalline sample averages over the resistivities in the  $ab$  plane and along the  $c$  axis where values at 300 K of  $\rho_{ab} \approx 250 \mu\Omega \text{ cm}$  and  $\rho_c \approx 4000 \mu\Omega \text{ cm}$  were reported by Analytis *et al.*<sup>32</sup> For the LaFePO crystal studied here (see Fig. 3), we find  $\rho_{ab} \approx 410 \mu\Omega \text{ cm}$ , where the experimental error in the absolute value is  $\pm 35\%$ .

#### IV. DISCUSSION

Our understanding of a given material is only complete if we are able to account for the changes which occur in its properties under variation of parameters such as the doping level, temperature, magnetic field, and pressure. Whereas temperature and magnetic field are “clean” parameters, the doping level and pressure are often less well defined. Doping may introduce lattice defects and strains and lack homogeneity over the lattice. Compared to doping, high pressure is viewed as a relatively clean parameter capable of varying properties on a single sample. However, not all pressures are created equal!

Ideally, applied pressure would be either purely hydrostatic (the pressure exerted by a fluid) or purely uniaxial. Unfortunately, these conditions can not be realized over a wide pressure/temperature range. A uniaxial pressure exceeding  $\sim 0.1 \text{ GPa}$  will likely irreparably damage the sample. With respect to hydrostatic pressure, a fluid under pressure will freeze into a solid as the temperature is lowered; solid pressure media exert shear stresses on a solid sample. However, the shear stresses exerted on a sample as the fluid freezes upon cooling are less significant than if the pressure were changed at a temperature where the pressure medium is frozen.

High-pressure experiments on the Fe-based superconductors have been carried out using a variety of pressure media, some fluid at room temperature, some solid, and in some cases no pressure medium at all was used. One should also consider that, for a given pressure medium, every high-pressure apparatus has its own characteristic behavior so that, for example, one piston-cylinder cell with Fluorinert pressure medium may have different pressure/temperature characteristics than another piston-cylinder cell with Fluorinert. The rate of cooling/warming before or after changing the pressure can also play a role on the results obtained. For samples such as the Fe-based superconductors, which have a high sensitivity

to strain, it is thus not surprising that the high-pressure experiments of different groups often give conflicting results on the same compound. As previously mentioned, He is the most hydrostatic pressure medium known. For the highly strain-sensitive Fe-based pnictides, then, He is clearly the pressure medium of choice.

In a He-gas apparatus, the pressure range is limited to  $\sim 1 \text{ GPa}$ . For higher pressures, a diamond-anvil cell can be loaded with liquid He to reach pressures approaching 1 Mbar. Should it not be possible to use He as pressure medium, studies using at least two different pressure media would reveal whether or not the pressure-dependent properties being studied are sensitive to shear strain.

We also point out that, if possible, high-quality single-crystalline samples should be chosen in quantitative studies of the hydrostatic pressure dependencies for layered materials such as the cuprates or the Fe-based pnictides. The reason is that in layered materials, the elastic properties are significantly anisotropic. If hydrostatic pressure is applied to a polycrystalline sample, the anisotropic response of every crystallite leads to a varying strain field across the grain boundaries between the crystallites. This does not occur with a single crystal.

The primary result of this paper is that for single-crystalline LaFePO, PrFePO, NdFePO and for polycrystalline LaFePO, the superconducting transition temperature  $T_c$  decreases rapidly under applied hydrostatic He-gas pressure to  $0.8 \text{ GPa}$ . This stands in contrast to the positive pressure derivative  $dT_c/dP$  observed in previous studies where less hydrostatic pressure media,<sup>13</sup> or no pressure media at all, were used (see Fig. 6 of the present study).<sup>12</sup> The present experiments thus give further evidence that the superconducting properties of the Fe-based pnictides are extraordinarily sensitive to lattice strains. In this class of materials, great care must be taken to minimize or eliminate lattice strain effects so that the “intrinsic” dependence of the properties on pressure is revealed.

That the Fe-based superconductors are highly sensitive to strain is supported by several previous studies. Duncan *et al.*<sup>19</sup> showed that an increasing uniaxial pressure component on  $\text{BaFe}_2\text{As}_2$  favors the appearance of superconductivity and may even be required to induce superconductivity. Recently, Zheng *et al.*<sup>33</sup> demonstrated that in  $\text{CaFe}_2\text{As}_2$ , superconducting precursors form above the bulk thermodynamic transition due to strains within the sample. Alireza *et al.*<sup>34</sup> found that  $\text{CaFe}_2\text{As}_2$ ,  $\text{SrFe}_2\text{As}_2$ , and  $\text{BaFe}_2\text{As}_2$  single crystals all become superconducting near  $0.3$ ,  $3$ , and  $3 \text{ GPa}$ , respectively, with Daphne Oil or Fluorinert as pressure medium. In a later experiment on a  $\text{CaFe}_2\text{As}_2$  single crystal using He-gas, however, Yu *et al.*<sup>15</sup> find no evidence for superconductivity to  $0.7 \text{ GPa}$ ! Kirshenbaum *et al.*<sup>17</sup> even find that well-annealed  $\text{SrFe}_2\text{As}_2$  single crystals do not superconduct at ambient pressure, but unannealed crystals, or crystals subjected to severe deformation, show evidence for superconductivity near  $21 \text{ K}$ . From their detailed studies on  $\text{SrFe}_2\text{As}_2$  single crystals, Saha *et al.*<sup>18</sup> conclude that there exists “an intimate relationship among superconductivity, magnetism, and crystallographic strain in this system of materials.” Further examples are given in a series of excellent reviews which include a discussion of high-pressure effects in the Fe-based pnictides.<sup>8,14</sup>

When applying even purely hydrostatic pressure to an Fe-based pnictide or a cuprate superconductor, several quantities change at the same time: the separation between the superconducting planes and their area both decrease; in addition, the doping level in the conducting planes varies. Fortunately, for small pressures ( $<1$  GPa), the change in doping level has a negligible effect on  $T_c$  if the sample is optimally doped. For such optimally doped Fe-based<sup>10,11,35</sup> and cuprate<sup>9</sup> superconductors, it has been shown through uniaxial pressure experiments that  $T_c$  increases appreciably if either the separation between the planes is *increased* or the area of the planes is *decreased*. The hydrostatic pressure dependence of  $T_c$  in a given tetragonal pnictide or cuprate is given by  $dT_c/dP = 2dT_c/dP_a + dT_c/dP_c$ . In both optimally doped pnictides and cuprates, the two partial-pressure derivatives nearly cancel, leaving a relatively small total hydrostatic pressure derivative  $dT_c/dP$ . The hydrostatic pressure derivative  $dT_c/dP$  has no direct physical significance since it represents the nearly complete cancellation of two large partial-pressure derivatives with opposite sign. It is thus clear that hydrostatic pressure measurements alone will not give the critical quantitative information needed to further our understanding of the high- $T_c$  materials. It is essential that hydrostatic pressure studies be combined with exacting uniaxial pressure measurements.

As a result of lanthanide contraction, the replacement of La in tetragonal LaFePO by Pr, Nd, Sm, and Gd progressively decreases both  $a$  and  $c$  lattice parameters. For example, for LaFePO, PrFePO, and NdFePO, the unit-cell volumes are 133.2, 127.7, and 126.2 Å<sup>3</sup>, respectively.<sup>2</sup> In view of the fact that  $T_c$  decreases under hydrostatic pressure for all three compounds (Fig. 4), is it possible that the decreasing values of  $T_c$  at ambient pressure for annealed crystals of LaFePO (6.71 K), PrFePO (3.97 K), and NdFePO (3.81 K) are simply a result of the lanthanide contraction (lattice pressure)?

Determining the change in  $T_c$  as uniaxial pressure is applied along the  $a$  and  $c$  directions would be the ideal way to test this hypothesis. As no uniaxial pressure studies are available, we consider whether lattice contraction along the  $a$  and  $c$  directions under applied hydrostatic pressure is similar to that under chemical pressure. The lattice is more compressible along the  $c$  axis by a factor of  $\kappa_c/\kappa_a \approx 1.8$ ,<sup>13</sup> where  $\kappa$  is the compressibility. Comparing the lattice parameters for these compounds, relative to LaFePO,  $c$  decreases about 1.65 and 1.66 times faster under chemical pressure than  $a$  for PrFePO and NdFePO, respectively.<sup>2</sup> Since the relative change in lattice parameters varies by less than 10% under applied and chemical pressure, it is possible to simply compare the unit-cell volumes in each case. Under hydrostatic pressure  $dT_c/dP \simeq$

$-2.46(7)$  K/GPa for LaFePO. Then, at about 1.1 and 1.2 GPa, the value of  $T_c$  for LaFePO would be the same as the ambient pressure  $T_c$  values for PrFePO and NdFePO, respectively. Now, the linear compressibility along each axis is given by  $\kappa_a = 2.74 \times 10^{-3}$  GPa<sup>-1</sup> and  $\kappa_c = 4.95 \times 10^{-3}$  GPa<sup>-1</sup>,<sup>13</sup> yielding the volume compressibility  $\kappa_v = 2\kappa_a + \kappa_c = 10.4 \times 10^{-3}$  GPa<sup>-1</sup>. Using this value of  $\kappa_v$ , the pressure required to reduce the unit-cell volume of LaFePO to that of PrFePO and NdFePO would be 4.4 and 5.8 GPa, respectively. These pressures are four to five times higher than those required to reduce the value of  $T_c$  for LaFePO to that of PrFePO or NdFePO. It seems clear, therefore, that the differences in  $T_c$  between these three compounds can not be accounted for by lanthanide contraction alone. This conclusion is supported by first-principles full-potential electronic-structure calculations of Vildosola *et al.*<sup>36</sup> who point out that the detailed band structure and Fermi surface of LaFePO depend very sensitively on small changes in both the interatomic distances and the bond angles within the iron-pnictogen subunit.

In summary, hydrostatic He-gas high-pressure ac susceptibility and resistivity studies on LaFePO, PrFePO, and NdFePO single crystals to 0.8 GPa demonstrate that the intrinsic dependence of  $T_c$  on pressure is large and negative, in contrast to results obtained in earlier studies under less hydrostatic pressure conditions. The present experiments thus provide further evidence for the sensitivity of the superconducting properties of the Fe-based pnictides to lattice strain effects and emphasize that great care must be taken to determine the “intrinsic” pressure dependencies. It is also stressed that combining the results of both hydrostatic and uniaxial pressure measurements is essential to reach a full understanding of how the superconducting state (including the pairing interaction) of the pnictides and cuprates depends on the interplanar and intraplanar spacings.

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