

## Pressure Effects in the Isoelectronic REFe<sub>0.85</sub>Ir<sub>0.15</sub>AsO System

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**S** Supporting Information

**ABSTRACT:** The effect of chemical and hydrostatic pressure has been studied systematically in a selected system belonging to the 1111 family of iron pnictide high-temperature superconductors. The results show a surprising similarity between the trend of critical temperature vs hydrostatic pressure for isoelectronic samples with different rare earths (RE) on the RE site and samples of the SmFeAsO<sub>1-x</sub>F<sub>x</sub> series with different doping levels. These results open new questions about the underlying mechanism for superconductivity in iron pnictides.

Soon after the discovery of superconducting iron pnictides<sup>1</sup> several high-pressure studies appeared in the literature. Most of them deal with the evolution of the critical temperature,  $T_C$ , as a function of an external hydrostatic pressure. A recent review about high pressure studies on iron pnictide superconductors can be found in ref 2. We concentrate our attention here on the REFeAsO (1111) systems. It has been shown that the application of an external pressure can induce a superconducting (SC) state in the undoped REFeAsO; for the LaFeAsO system, for example, a SC state occurs at around 2 GPa. With increasing pressure,  $T_C$  rises suddenly to a maximum value of about 20 K, followed by a plateau up to about 10–12 GPa, and by a slow  $T_C$  drop above ~15 GPa.<sup>3</sup> In the case of F-doped 1111 iron pnictides, the application of an external pressure can increase the  $T_C$  up to a certain  $P$ -value after which the  $T_C$  starts to decrease.<sup>2</sup>

Besides the effects induced by external pressure, another way of modulating the interatomic distances is the chemical pressure effect induced by chemical substitution of elements with different ionic radii. Such a way of tuning the properties of iron pnictides has been used to enhance the critical temperature of 1111 iron pnictides but was not investigated in a very systematic way. In

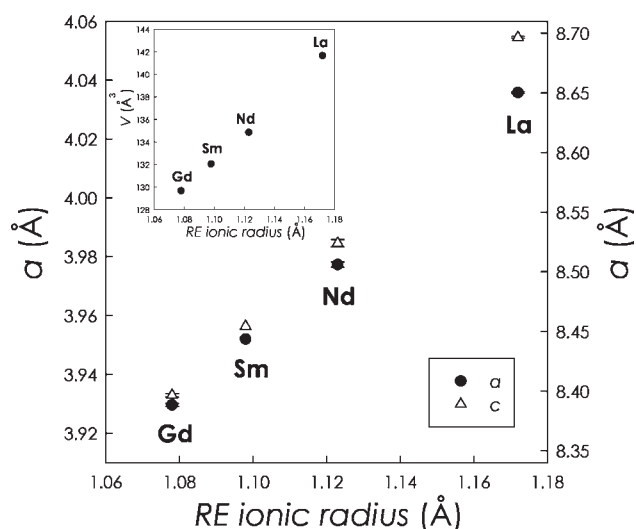
addition, a comparison between the role of chemical and external pressure is of great relevance in order to understand the importance of chemical substitution in these systems and sheds further light on the underlying mechanism for superconductivity in iron pnictides.

In this communication we are reporting a study of the chemical pressure effect in a 1111 iron pnictide system together with the investigation of the effect of an external pressure on some selected samples. We chose as a “model” system the REFe<sub>0.85</sub>Ir<sub>0.15</sub>AsO compounds where RE = La, Nd, Sm and Gd. We have recently investigated the SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO pnictide as a function of doping,<sup>4</sup> and we are currently studying the phase diagrams of the other solid solutions with different RE. Superconductivity in the REFeAsO compounds is induced by Ir-doping levels from about 5–7% up to 20% with maximum critical temperatures at  $x \approx 10\%$  with a wide range of compositions where the  $T_C$  retains its maximum value in a plateau-like behavior. The trend of  $T_C$  vs Ir-doping closely resembles the trend of  $T_C$  vs  $P$  of undoped REFeAsO, as we have stressed in ref 4.

The REFe<sub>0.85</sub>Ir<sub>0.15</sub>AsO system has been chosen among other possible systems for several reasons: (i) because it allows a strict control of samples stoichiometry during the synthesis thus allowing to get reliable correlations between composition and experimental data (which is not always easy in F-doped systems as discussed in refs 5 and 6); (ii) the trend of  $T_C$  and structure with Ir-doping in the single REFe<sub>1-x</sub>Ir<sub>x</sub>AsO systems strongly suggests the fundamental role of structural variation over the electronic doping; (iii) the evidence that in the SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO series is found the highest  $T_C$  among all the transition-metal (TM) doped 1111 iron pnictides further motivated the search of even higher  $T_C$  in analogous systems.<sup>4,7</sup>

**Received:** November 3, 2010

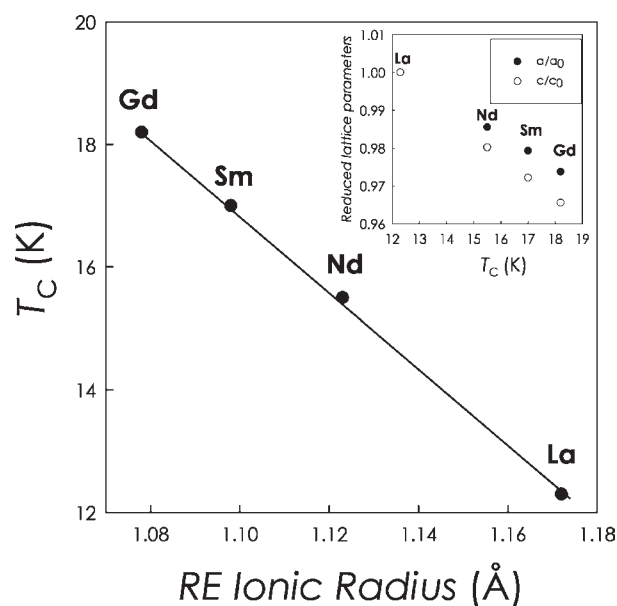
**Published:** February 22, 2011



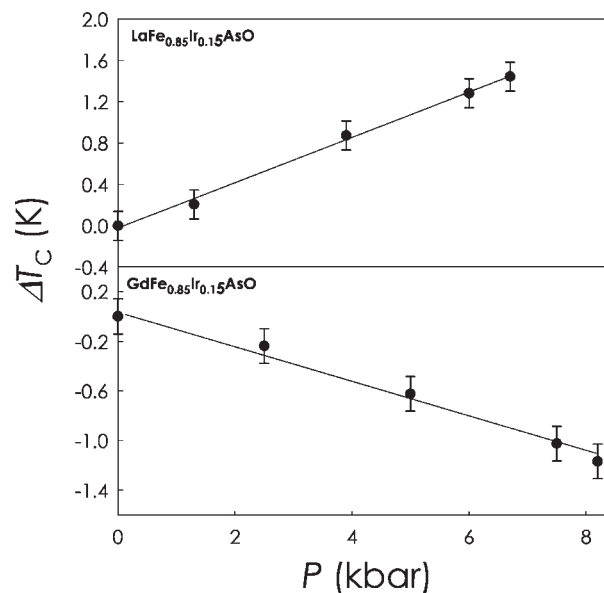
**Figure 1.** Lattice parameters and unit cell volume (inset) as a function of the RE size for the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (RE = La, Nd, Sm and Gd) samples.

Polycrystalline samples with composition  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (RE=La, Nd, Sm and Gd) have been synthesized as described in ref 4. Samples resulted to be single phase with impurity levels—where present—below 3–4% (see Supporting Information [SI]) Structural parameters have been determined by means of Rietveld refinement of X-ray diffraction patterns acquired on a Bruker D8 Advance instrument.  $T_C$  and the external pressure effects on  $T_C$  have been determined by means of SQUID measurements in a Quantum Design instrument. For the pressure measurements, the samples were mixed with Fluorinert FC77 (pressure transmitting medium) with a sample to liquid volume ratio of approximately 1:6. The pressure was generated in a copper–beryllium piston cylinder clamp, which allows reaching hydrostatic pressures up to about 1.2 GPa.<sup>8</sup> The value of the pressure was measured in situ by monitoring the  $T_C$  shift of a small piece of In included in the pressure cell. High pressure X-ray diffraction data were collected on the ID09 beamline at the ESRF Facility in Grenoble with a diamond anvil cell (DAC). The beam ( $\lambda = 0.414740 \text{ \AA}$ ) size on the sample is normally about  $30 \times 30 \mu\text{m}^2$ . A DAC was employed with low-fluorescence IA, 350- $\mu\text{m}$  culet diamonds. The samples were finely milled and a high-pressure DAC loading, with He as pressure transmitting medium, was performed. The image plate detector is a Mar345 reader.

Figure 1 presents the trend of lattice parameters and cell volume (inset) as a function of the RE-size (same coordination) for the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (RE = La, Nd, Sm and Gd) samples. At room temperature all the samples display the tetragonal  $P4nmm$  symmetry usually found in 1111 iron pnictides. As can be appreciated from Figure 1 the unit cell volume expands in a linear way as the size of the RE increases. The same behavior is found for the  $a(b)$  and  $c$  lattice parameters. Also the bond lengths (see the SI) show a linear expansion along with the RE size increase except for the Fe–As bond length which keeps a more or less constant value irrespective to the size of the rare earth. This is due to the  $z$ -As value which, contrary to the  $z$ -RE value, linearly decreases as the RE ionic radius increases from 0.6606(9) for  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  to 0.6440(9) for  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (see the SI). Finally, the Fe–As–Fe bond angle ( $\alpha$ ) moves from  $116.37(5)^\circ$  for La to  $111.09(4)^\circ$  for Gd.



**Figure 2.**  $T_C$  as a function of the RE size for the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (RE = La, Nd, Sm and Gd) samples. Inset: trend of reduced lattice parameters as a function of superconducting critical temperature.



**Figure 3.**  $\Delta T_C$  as a function of pressure for the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  samples.

Figure 2 shows the trend of  $T_C$  determined from the SQUID measurements ( $T_{\text{onset}}$ ) carried out on the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (RE = La, Nd, Sm and Gd) samples. The variation of the critical temperature is perfectly linear as a function of the RE size, and in particular, it increases as the ionic size decreases. Such a correlation in an *isoelectronic* 1111 iron pnictide system has not been observed before. The substitution on the RE–O layer reduces the chemical composition effect to the minimum, leaving, as unique parameter affecting the material properties, the *chemical pressure effect* induced by the change of the RE size. The close correlation between structural effects and critical temperature can be further assessed by looking at the inset of Figure 2 where

the  $a/a_0$  and  $c/c_0$  parameters as a function of the critical temperature are plotted. We also stress that the  $T_C$  found for the  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  is the highest ever reported for a TM-doped 1111 iron pnictide.

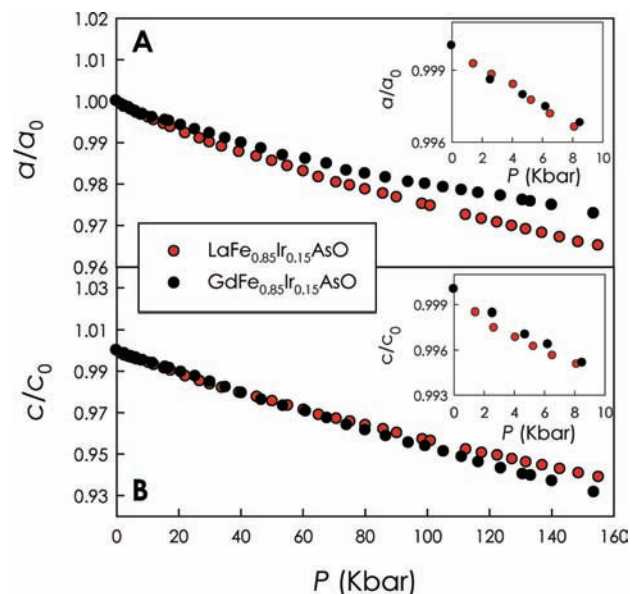
In order to further explore the  $T_C$  behavior vs. pressure of  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  (RE = La, Nd, Sm and Gd) samples, high-pressure SQUID measurements were collected on the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  compositions selected as being the two extremes in the series investigated.

Figure 3 shows the trend of change in the superconducting critical temperature [defined as  $\Delta T_C = T_C(P_i) - T_C(P_0)$ , where  $T_C(P_i)$  is the critical temperature at a defined pressure at which the measurement is carried out, while  $T_C(P_0)$  is the critical temperature at ambient pressure] as a function of pressure for the two compositions investigated. As can be seen, both samples respond to pressure very sensitively, with the  $T_C$  shifting in a linear way but with opposite slopes at a rate of  $+0.24$  K/kbar for the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $-0.14$  K/kbar for  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$ . Very interestingly, these two values are, within the estimated standard deviation, the same rates found for the  $\text{SmFeAsO}_{0.90}\text{F}_{0.10}$  ( $+0.26(2)$  K/kbar) and  $\text{SmFeAsO}_{0.80}\text{F}_{0.20}$  ( $-0.144(5)$  K/kbar).<sup>9</sup>

The observation of nearly equal pressure dependencies for samples in the  $\text{SmFeAsO}_{1-x}\text{F}_x$  and  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  systems is of great significance. In the first case the samples are characterized by different electron doping levels but substantially similar structural parameters (the change of  $a(b)$  and  $c$  lattice parameters as a function of F-doping is small, i.e. the volume changes of about 0.8% passing from  $x = 0$  to  $x = 0.20$ )<sup>10</sup> and in particular the  $x = 0.10$  sample (with  $T_C$  around 18 K) can be considered in the under-doped regime while the  $x = 0.20$  sample (with  $T_C$  around 50 K) is in the optimal-doping regime. In the other case, the samples of the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  system can be considered in the optimal-doping regime for all the RE and they strongly differ each other for what concerns the structural parameters (for example, the unit cell volume reduces of about 8% going from La to Gd, i.e. 10 times more with respect to the change passing from  $x = 0$  to  $x = 0.20$  in the  $\text{SmFeAsO}_{1-x}\text{F}_x$  system). In addition, all the samples of the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  series are isoelectronic.

In order to further investigate the pressure effect on the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  system, we carried out high-pressure X-ray diffraction on those two samples for which high pressure SQUID data have been collected. Figure 4 shows the trend of reduced lattice parameters as a function of pressure in the whole investigated range, while the insets report the trend in the  $P$ -range analogous to that of HP SQUID data.

Looking at the  $P$ -range of the SQUID measurements (insets of Figure 4) it can be seen that for both the  $a/a_0$  and  $c/c_0$  parameters the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  samples behaves in the same way as a function of pressure. The changes of the lattice parameters in the 0–10 kbar range are extremely small and of the order of 0.3% for both samples. Significant differences in the relative compressibilities can be only observed for higher pressure ranges and in particular for the  $a/a_0$  parameter. In addition, that the relative trend of the reduced lattice parameters is different (at high pressure) for the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  samples with the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  having a higher compressibility along the  $c$ -axis and a smaller along the  $a(b)$ -axis while the opposite occurs for the  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  sample. The HP structural data in the  $P$ -range of magnetization measurements clearly show that the difference in the  $\Delta T_C$  trend presented in Figure 3 for the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  samples



**Figure 4.** Trend of reduced lattice parameters  $a/a_0$  (panel A) and  $c/c_0$  (panel B) as a function of pressure for the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  and  $\text{GdFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  samples. Insets: same data in the 0–10 kbar range.

cannot be related to difference in the relative variation of the lattice parameters vs.  $P$  but that this effect is due to the initial chemical pressure effect induced by the different RE-size. The HP X-ray diffraction data can be also used to compare the effect of external and chemical pressure on the samples. Let us consider the  $\text{LaFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  high pressure structural data of Figure 4 (see also the Supporting Information) and the relative lattice parameters vs. RE-size reported in the inset of Figure 2. In both cases the pressure has an anisotropic effect on the compressibilities along the  $a(b)$ - and  $c$ -axis with the latter being compressed more. By comparing the values of  $a/a_0$  and  $c/c_0$  it turns out that  $P$ -values corresponding to the smaller  $a/a_0$  value (Gd) of the inset of Figure 2 is obtained by applying an external hydrostatic pressure of about 108 kbar, while for the  $c/c_0$  parameter it corresponds to a value around 75 kbar. Interesting evidence is that the chemical pressure has a more anisotropic effect on the lattice parameters with respect to the hydrostatic pressure, thus compressing in a more efficient way the  $c$  lattice parameter.

The change in the  $dT_C/dP$  in the  $\text{SmFeAsO}_{1-x}\text{F}_x$  has been interpreted as a crossover of the quantum critical point owing to the competition of spin density wave order and superconductivity as the  $F$ -content (electron doping) increases.<sup>9</sup> In the case of the  $\text{REFe}_{0.85}\text{Ir}_{0.15}\text{AsO}$  system the electronic doping does not change passing from La to Gd, while a significant compression of the crystal structure (in particular along the  $c$ -axis) occurs which is different with respect to an external hydrostatic pressure. In this case the change in the  $dT_C/dP$  trend is caused by a structural effect alone without electronic doping or chemical disorder or differences in the compressibilities. However, the results presented suggest a similarity in the evolution of the  $dT_C/dP$  behavior as a function of electron doping and chemical pressure in an isoelectronic pnictide system, which opens new perspectives about the role of pressure on the competing interactions in 1111 iron pnictides. These results should stimulate a substantial theoretical investigation in order to unveil the relative role of electron doping and pressure effects which may reveal new ways of playing with these two parameters.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Structural data for the RE-Fe<sub>0.85</sub>Ir<sub>0.15</sub>AsO (RE = La, Nd, Sm and Gd) samples. Plots of lattice parameters and volume change as a function of pressure for LaFe<sub>0.85</sub>Ir<sub>0.15</sub>AsO and GdFe<sub>0.85</sub>Ir<sub>0.15</sub>AsO samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

We gratefully acknowledge funding from CARIPLO Foundation (Project 2009-2540 “Chemical Control and Doping Effects in Pnictide High-temperature Superconductors”). ESRF is acknowledged for providing beam time.

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