

LETTER

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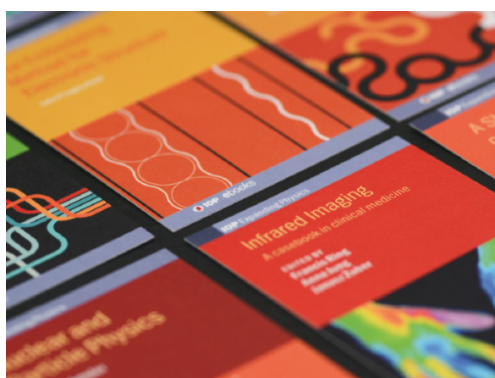
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# P-T phase diagram of iron arsenide superconductor $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$

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**Abstract** –  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  belongs to the recently discovered family of *high- $T_C$*  iron-based superconductors. We have studied the influence of high pressure on transport properties of this material at low temperatures using the four-probe electrical conductivity technique in a diamond cell. Contrary to La-based compounds, we did not observe a maximum in  $T_C$  under pressure. Under compression,  $T_C$  drops rapidly as a linear function of pressure with the slope  $k = -2.8 \pm 0.1 \text{ K/GPa}$ . Under decompression, the behavior is completely reversible. The extrapolated value of  $T_C$  at zero pressure is about  $T_C(0) = 51.7 \pm 0.4 \text{ K}$ . At pressures higher than  $\sim 18.4 \text{ GPa}$ , the superconducting state disappears at all measured temperatures, although electrical resistance changes slope dramatically and shows a concave behavior. These observations may be related to the Kondo effect or to a weak localization of two-dimensional carriers at high pressures and low temperatures below  $\sim 45 \text{ K}$ , indicating a competition mechanism with the superconducting phase. On the bases of our experimental data, we propose a tentative *P-T* phase diagram of  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$ .

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**Introduction.** – The very sharp increase of  $T_C$  in the recently discovered family of *high- $T_C$*  pnictide superconductors (with chemical formula  $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ , see refs. [1–3], where RE is the rare-earth element) over a period of a few months gave hope for producing *high- $T_C$*  superconducting materials suitable for practical industrial applications. One important feature of these new materials is their very good ductility, which can make the manufacturing of superconducting wires for electrical applications easier (contrary to the brittle copper oxide *high- $T_C$*  superconductors). Another very important advantage is the high value of the upper critical field in iron

pnictides [4]. Previous studies have shown that changes in rare-earth ions or application of high pressure [2,3] have a substantial influence on the interatomic distances of the lattice. Starting from the light rare-earth element,  $T_C$  increases substantially towards the substitution of Nd and Sm ions [3]. A similar behavior of  $T_C$  was observed due to the compression of the lattice [2]. Such similarity is expected because these perturbations change interatomic distances. Significant theoretical and experimental efforts have been carried out to elucidate the mechanism of the superconducting (SC) pairing, in which the exchange of itinerant spin-fluctuations may play a dominant role (see reviews [5] and references therein). The order parameter symmetry in the spin-fluctuation theories for lightly and

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moderately doped materials relates to the sign-changing  $s$ -wave ( $s\pm$ ) [6], which has been confirmed by a number of experimental studies [5]. This is quite different from the  $d$ -wave cuprate superconductors in which the spin pairing mechanism remains mysterious. A variety of working models have been proposed including antiferromagnetic fluctuations as described in the framework of the  $t$ - $J$ -type models. A conclusive explanation of the pairing mechanism in cuprates has yet to be presented, however. An interesting idea linking both classes of superconductors was outlined in a recent review by Grant [7] that states that cuprates and pnictides exhibit dual-system behaviors which share common features of the correlated electron system with the cuprates being a strongly correlated system and the iron pnictides being more itinerant. Therefore, understanding the nature of superconductivity in iron pnictides would shed new light on uncovering the mystery of the high- $T_C$  cuprates.

The structure of  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  is  $P4/nmm$ , similar to other materials in this family [1,3,8]. Like cuprates, pnictides exhibit a layered structure.  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  has Nd-O layers in which a small fraction of oxygen ions are substituted by F ions to induce carriers in the conducting Fe-As layers. It has been shown [3] that oxygen vacancies in Nd-O layers can also serve as a source of electrons instead of having to add fluorine. Fe-As conducting layers are crimped contrary to the nearly planar Cu-O layers in cuprates. Nevertheless, some experiments have established similarities between pnictides and cuprates [9,10]. For example, a similar  $3\text{D} \rightarrow 2\text{D}$  crossover behavior was found in the vortex structure [10]. While it is widely believed that superconductivity occurs in the Fe-As layer that is common to all iron pnictides, it remains unclear as to why  $T_C$  varies so much in various pnictide systems (*e.g.*, 1111, 122, and 111) or even within one family. Several early systematic structure studies [11] suggested that structural parameters, such as the Fe-As-Fe bond angle or the As height ( $h_{\text{As}}$ ) above the Fe square lattice, may play a significant role in the  $T_C$  variation. First principles DFT (density functional theories) [12] and spin-fluctuation calculations [13] confirmed the important role of the structural parameter  $h_{\text{As}}$  in the superconducting state. These types of theoretical approaches are used to understand how the variation of  $h_{\text{As}}$  affects  $T_C$ . In real materials, however, the As height is not a free parameter and can be significantly influenced by changing the chemical composition. One of the better ways to study the dependence of  $T_C$  on the structure is to apply external pressure on one particular material. The 1111 family of pnictides has shown to be especially promising in this respect because it contains only one Fe-As layer per unit cell and thus is a simpler case than other systems such as the 122 system. A number of high-pressure studies have been carried out on this family [14,15]. Optimally doped Nd-based pnictide has a high  $T_C$  among the members of its family.  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  thus represents an interesting case for understanding the high  $P$ - $T$  phase diagram of the system.

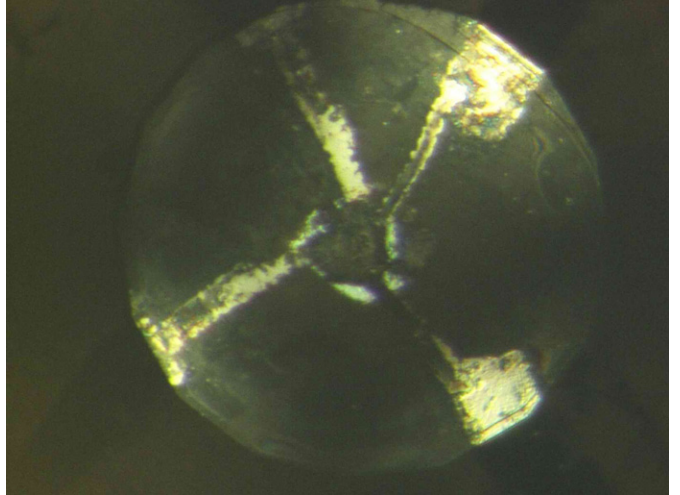


Fig. 1: (Colour on-line) Image of the  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  sample in a four-probe resistivity measurement in a diamond anvil cell having  $300\ \mu\text{m}$  culets, NaCl pressure medium, cBN gasket, and a sample chamber of approximately  $80\ \mu\text{m}$  diameter. The opaque  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  sample is located in the very center of the picture. Four Pt foil leads are connected to the opaque sample in the center of the gasket hole using NaCl medium. The pressure is about 10 GPa.

**Experimental procedure.** – High-pressure–low-temperature resistivity measurements were carried out with the superconductor  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  in a diamond anvil cell. We used a miniature nonmagnetic cell [16] specially designed for measurements at low temperatures and under hydrostatic conditions [17]. We used an insulating gasket made of a mixture of cubic boron nitride with epoxy [18]. Sodium chloride was used as a pressure medium.

The pressure was measured through the ruby fluorescence technique. Several ruby chips with dimensions of about  $1\ \mu\text{m}$  were placed into the cell along with the sample at various locations in the sample chamber in order to evaluate pressure gradients in the chamber; measured pressure gradients were typically less than 2 GPa at all experimental pressures. In fig. 1 we show an image of the  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  sample in a diamond anvil cell [16]. Four platinum foil leads with an initial thickness of about 1 micron and a width of about 10–15 microns were used for the 4-probe measurements.

**Results and discussion.** – In fig. 2 we show temperature-dependent resistances measured by the four-probe method at high pressures during compression (fig. 2(a)) and decompression (fig. 2(b)). The resistance has been normalized to  $R_{\text{min}}$ , the resistance at the minimum point in the  $R(T)$  dependence. In fig. 3 we show the pressure dependence of  $T_C$ . The  $T_C$  values were determined from the onset of the superconducting transition in the  $R(T)$  dependence curves at different pressure points. The dependence is linear and can be

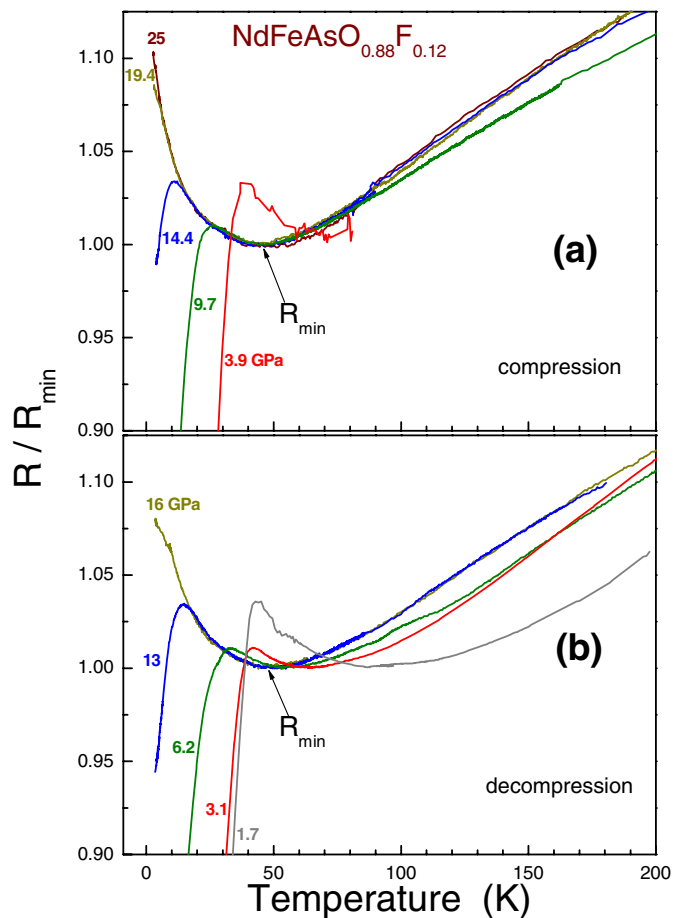


Fig. 2: (Colour on-line) Electrical resistance of the  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  sample as a function of temperature at various pressures.

extrapolated to about 18.4 GPa where  $T_C$  is zero:

$$T_C = T_C(0) + k \cdot P \quad (1)$$

where  $T_C(0) = 51.7 \pm 0.4 \text{ K}$ , and  $k = -2.8 \pm 0.1 \text{ K/GPa}$ .

Below  $T \sim 45 \text{ K}$ , the resistance curve changes slope and reveals a concave behavior with decreasing temperature. Such concave behavior before the transition into a superconducting state has been found in several pnictides [3,9,15,20], which usually results from a partial dielectrization due to the formation of the spin-density wave (SDW) state. Nevertheless, in our case there is no evidence for the presence of the SDW state at ambient pressure. Another reason for the steep increase of the resistance may be due to the Kondo effect, which has been discussed recently for  $\text{NdFeAsO}_{0.7}\text{F}_{0.3}$  single crystals irradiated by  $\alpha$ -particles [21]. Our samples belong to the same Nd-1111 family with a smaller F concentration. An additional possible explanation of the resistance change may be a result of the weak localization due to the scattering on the statically and randomly distributed impurities [22]. These possibilities are discussed in details below.

In fig. 4 we show the temperature dependence of the resistance measured at different pressures in the form

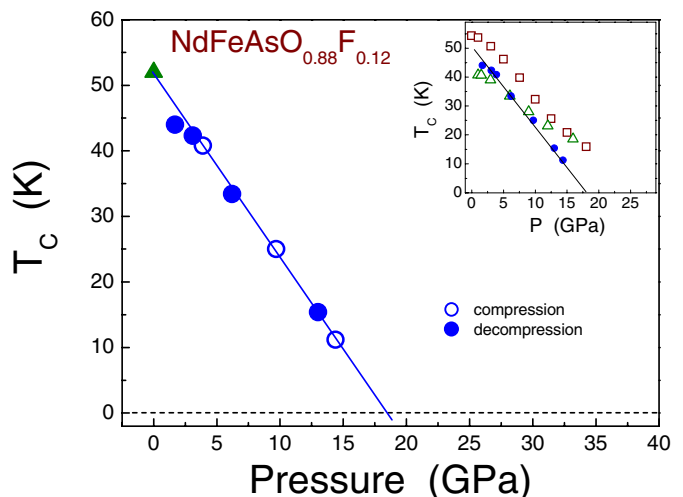


Fig. 3: (Colour on-line) Pressure-dependence of  $T_C$  in the  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  sample. Experimental data shown in colored circles can be linearly extrapolated to zero at about 18.4 GPa. The green triangle represents the ambient pressure value (from ref. [3]). The inset shows our data (filled blue circles) in comparison with the data for  $\text{FeAsNdO}_y$  from refs. [15,19] for  $y = 0.6$  (open squares) and for  $y = 0.8$  (open triangles).

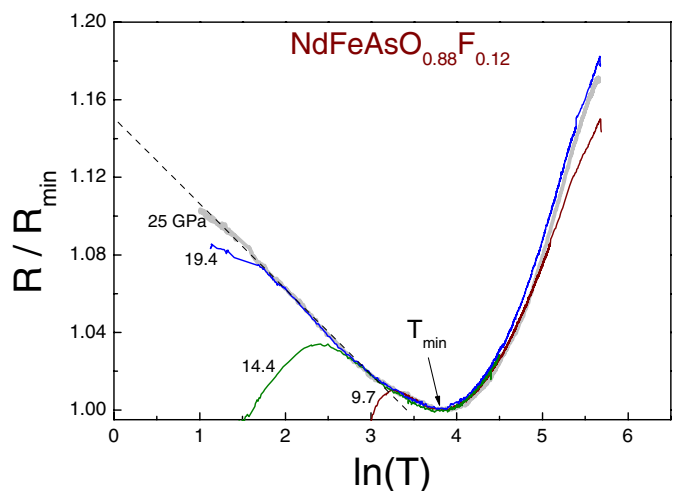


Fig. 4: (Colour on-line)  $R/R_{\min}$  as a function of  $\ln T$  at various constant pressures.

$R/R_{\min}$  vs.  $\ln T$ . There is a linear part of this dependence at 25 GPa in the range 2.8–45 K with a minimum  $R_{\min}$  at  $T_{\min}$ . We fitted the experimental data in fig. 4 using:

$$R/R_{\min} = A - B \ln T \quad (2)$$

with  $A = 1.15$ ,  $B = 0.043$ , and  $T$  being the temperature in kelvins. Note that the behavior of  $T_C$  and  $R(T)$  is completely reversible in decompression.

The superconducting transition temperature  $T_C$  in the Nd-based sample decreases under compression following the linear pressure dependence. The extrapolated pressure corresponding to  $T_C = 0$  is about 18.4 GPa. Several unusual features were observed in the pressure-induced

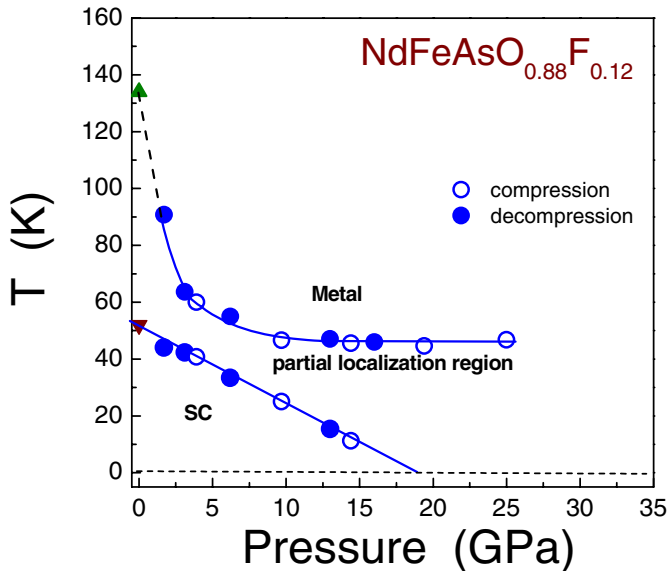


Fig. 5: (Colour on-line)  $P$ - $T$  phase diagram of the iron arsenide  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$ . The line between a normal metal above  $T_{\min}$  and a metallic state with the partial localization of charge carriers below  $T_{\min}$  was deduced from the pressure dependence of the minimum position ( $T_{\min}$ ) in the  $R$ -*vs.*- $T$  curve. The solid green triangle-up represents the onset of the spin-density wave in pure  $\text{LaOFeAs}$  at ambient pressure (from ref. [23]). The solid red triangle-down represents the  $T_C$  at ambient pressure from ref. [3].

behavior of  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$ . The first one is the extremely rapid drop of  $T_C$  under pressure (fig. 3). The pressure slope of  $T_C$  is equal to  $-2.8 \pm 0.1$  K/GPa. Similar experiments have been conducted by other groups on Nd-based pnictides with different oxygen deficiency [15,19,24]. The results of these studies are shown in the inset of fig. 3, together with our data for comparison. It is clearly seen that our samples demonstrate the maximal slope of the  $T_C$  decrease under pressure. The second unusual feature is the observed anomaly in the temperature behavior of resistance before the transition into the SC state.

As to the significant increase in the resistance with decreasing temperature, one of the possible explanations can be related to the Kondo effect [3]. Magnetic impurities are inevitably present in most transition metal compounds, *e.g.*, other rare-earth elements admixed to Nd. The  $R(T)$  minimum at  $T = T_{\min}$  is known to result from a competition of two contributions in the bulk resistivity [21,25]

$$\rho = \rho_v + c_m a \ln(\mu/T) + bT^5, \quad (3)$$

where  $\rho_v$  is the residual resistivity. The second term of the equation reflects the Kondo-effect contribution depending on the concentration of magnetic impurities  $c_m$  and the chemical potential  $\mu$ , while the last term stems from the electron-phonon scattering at low temperatures.  $a$  and  $b$  in the equation are phenomenological parameters.

Minimization of eq. (3) results in

$$T_{\min} = (c_m a / 5b)^{1/5} \quad (4)$$

The weak (power) dependence of  $T_{\min}$  on material parameters  $c_m$ ,  $a$ , and  $b$  explains the weak dependence of the  $T_{\min}$  on pressure in the phase diagram (fig. 5). The parameter  $a$  is related to the Kondo temperature  $T_K$  as [25]

$$a \sim 1/(\mu/T_K) \quad (5)$$

The success of the linear fit (2) in the experimental temperature range  $T = 2.8$ – $45$  K proves that  $T_K \ll T$ . Our estimations give  $T_K \leq 10^{-1}$ – $10^{-2}$  K.

An additional mechanism that may result in the resistivity turn-up and  $\ln T$  dependence for two-dimensional carriers is related to the quantum corrections to the conductivity in dirty metals [22]. The quasi-two-dimensional character of carriers is an essential property of pnictides. Here we do not have enough information to determine whether the Kondo effect or the weak localization scenario plays a major role in the system. Nevertheless, both effects can result in the partial localization of the carriers below  $T_{\min}$ .

**Summary.** – In summary, we have investigated high-pressure effects on the properties of  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$  high- $T_C$  superconductor at low temperatures. The critical temperature  $T_C$  drops linearly with the slope of  $-2.8 \pm 0.1$  K/GPa. The extrapolated value of  $T_C$  at zero pressure is equal to  $51.7 \pm 0.4$  K, close to the ambient pressure value. We suggest that at pressures higher than  $\sim 18.4$  GPa the superconducting state is destabilized at all temperatures. Before the transition into the superconducting state there is an evidence of the transition into the unusual state with partial electron localization. Based on these findings, we have presented a new  $P$ - $T$  phase diagram of the high- $T_C$  superconductor  $\text{NdFeAsO}_{0.88}\text{F}_{0.12}$ .

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