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EPL, 88 (2009) 47008

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Superconductivity at 31 K in the “111”-type iron arsenide superconductor $\text{Na}_{1-x}\text{FeAs}$ induced by pressure

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received 3 June 2009; accepted in final form 2 November 2009

published online 2 December 2009

PACS 74.20.Mn – Nonconventional mechanisms (spin fluctuations, polarons and bipolarons, resonating valence bond model, anyon mechanism, marginal Fermi liquid, Luttinger liquid, etc.)

PACS 74.62.Fj – Pressure effects

PACS 74.25.Dw – Superconductivity phase diagrams

Abstract – The effect of pressure on the superconductivity of “111”-type $\text{Na}_{1-x}\text{FeAs}$ is investigated through temperature-dependent electrical-resistance measurements in a diamond anvil cell. The superconducting transition temperature (T_c) increases from 26 K to a maximum of 31 K as the pressure increases from ambient pressure to 3 GPa. Further increasing pressure suppresses T_c drastically. The behavior of pressure-tuned T_c in $\text{Na}_{1-x}\text{FeAs}$ is much different from that in Li_xFeAs , although they have the same Cu_2Sb -type structure.

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Introduction. – The discovery of superconductivity at 26 K in $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ [1] by Prof. Hosono opens a new era for high-temperature superconductor research. The T_c of this material was further raised to 55 K at ambient pressure by replacing La with other rare-earth ions with smaller radius [2,3]. The transition temperature is only second to the high- T_c cuprate superconductors. Subsequently, superconductivity with a relative high transition temperature T_c was found in several other “1111”-type iron pnictide compounds [4–6]. Other than the aforementioned “1111”-type compounds (REFeAsO , RE = rare earth), the “122”-type BaFe_2As_2 with a tetragonal ThCr_2Si_2 -type structure was found to be superconducting at 38 K by hole doping [7]. More recently, we found Li_xFeAs , a “111”-type iron arsenide compound with a Cu_2Sb -type tetragonal structure, to be superconducting with a transition temperature of 18 K [8]. With element substitution, the isostructural $\text{Na}_{1-x}\text{FeAs}$ was also found to be superconducting with $T_c = 9\text{--}26$ K [9–11] at ambient pressure. Different from the “1111”-type or “122”-type compounds, the spin density wave (SDW) transition seems absent in Li_xFeAs , as derived from experimental

observations [8,12,13]. The pressure-tuned superconductivity has been investigated for many iron arsenide compounds to enhance the superconductivity transition temperature as well as to understand the mechanism of superconductivity in iron arsenide superconductors. It has been found that pressure enhanced its T_c to 43 K right after the discovery of superconductivity in $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ [14]. For some “1111”-type and “122”-type parent compounds, the superconductivity can be initiated by pressure and the T_c can be pushed to a maximum value with initial compression, then the T_c decreases at higher pressure region, *e.g.* for LaFeAsO [15] and AFe_2As_2 (A = Sr, Ba) [16,17]. For doped REFeAsO_{1-x} with smaller RE ion radius, the T_c is suppressed monotonously with increasing pressure [18,19]. The T_c is also suppressed linearly with pressure for the “111”-type Li_xFeAs [20–22]. More recently, $\alpha\text{-FeSe}$, with a structure composed of anti-PbO-type FeSe layers, was found to exhibit superconductivity at about 8 K at ambient pressure [23] and showed a dramatic enhancement of T_c by applying low pressure [24,25]. Pressure is therefore a very important parameter to study iron pnictide superconductors. Here we report the pressure effects on superconductivity of “111”-type $\text{Na}_{1-x}\text{FeAs}$. The results are compared with those for the isostructural superconductor Li_xFeAs .

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Experimental details. – The $\text{Na}_{1-x}\text{FeAs}$ compound used in the experiment was synthesized by the solid-state reaction method using Na_3As , Fe and As as starting materials following the method described in ref. [8]. Considering volatility loss of Na in the sintering process, the Na_3As precursor powder, Fe and As powder were mixed according to mole ratio of $\text{Na}:\text{Fe}:\text{As} = 1.2:1:1$ that would give rise to a pure “111”-type structural sample with some sodium vacancies. The mixture was pressed into pellet and wrapped with Ta foil in a glove box with high purity argon atmosphere. The pellet wrapped by the Ta foil was then sealed under vacuum in a quartz tube and sintered at 800°C for 20 hours. The resulting sample was characterized by X-ray powder diffraction with a Mac Science diffractometer. Diffraction data was collected with 0.02° and 15 s/step. The composition of the sample was analyzed using an inductively coupled plasma (ICP) spectrometer. The results were $\text{Na}:\text{Fe}:\text{As} = 0.86:1:1$ indicating there exist vacancies at the sodium site that contribute to generate carriers [9,11].

The pressure-induced evolution of the superconducting transition in $\text{Na}_{1-x}\text{FeAs}$ was investigated by four-probe electrical-resistance measurement methods in a diamond anvil cell (DAC) at variant pressures. In our experiment, pressure was generated by a pair of diamonds with $600\ \mu\text{m}$ -diameter culet. The stainless-steel gasket was pre indented from $250\ \mu\text{m}$ to $\sim 40\ \mu\text{m}$ thickness before drilling a $250\ \mu\text{m}$ hole in the center that served as the sample chamber. The sample hole was covered with a thin layer of cubic boron nitride (BN) for electrical insulation between the gasket and the electrodes. Gold wires of $18\ \mu\text{m}$ diameter were used as electrode leads. The $\text{Na}_{1-x}\text{FeAs}$ sample was laid in the center of the four electrodes with pressure media around. The sample size was about $200\ \mu\text{m} \times 100\ \mu\text{m} \times 20\ \mu\text{m}$. MgO fine powder was used as the pressure-transmitting medium in the experiment. The pressure was measured at room temperature by the ruby fluorescence method before and after each temperature cooling-down. The highly hygroscopic nature of the $\text{Na}_{1-x}\text{FeAs}$ sample makes it very difficult to get a good electric contact when preparing the electrodes in air. We prepared the electrodes as fast as possible (less than 30 min) to reduce the reaction time of the sample surface with water.

Results and discussion. – The diffraction pattern of the $\text{Na}_{1-x}\text{FeAs}$ sample can be indexed by the Cu_2Sb -type structure with $P4/nmm$ symmetry, as shown in fig. 1, isostructural with Li_xFeAs [8]. Figure 2 shows the electric resistance of $\text{Na}_{1-x}\text{FeAs}$ as a function of temperature at different pressures up to 8 GPa. It also shows that the superconducting transition becomes sharper with initial increasing pressure and gets broader at higher pressures. This behavior is probably related to the reactive nature of the $\text{Na}_{1-x}\text{FeAs}$ sample. The broader transition width at ambient pressure is also observed by other groups (ref. [11]). The increased pressure gradient at higher

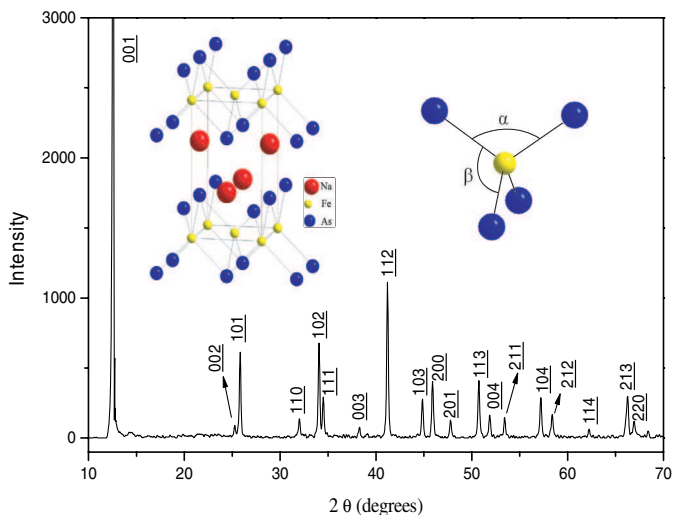


Fig. 1: (Color online) X-ray diffraction spectrum of the polycrystalline sample with nominal composition $\text{Na}_{1.2}\text{FeAs}$. The $\text{Na}_{1-x}\text{FeAs}$ crystallizes into the Cu_2Sb -type structure with space group $P4/nmm$. The large (red) spheres are Na atoms, the medium (blue) spheres are As atoms, and the small (yellow) spheres are Fe atoms.

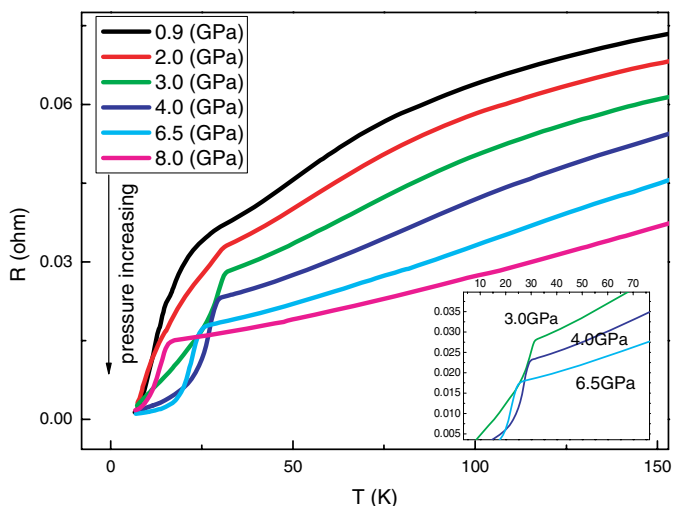


Fig. 2: (Color online) The temperature dependence of resistance for $\text{Na}_{1-x}\text{FeAs}$ superconductor at variant pressures from 0 GPa to 8 GPa; The insert shows the details of superconductivity transition with pressure from 3 GPa to 6.5 GPa.

pressure region causes the broadening of the resistance transition.

The T_c values at variant pressures are determined from the initial deviation from the extrapolated line of the R - T curve as shown in fig. 3. The pressure dependence of T_c of the $\text{Na}_{1-x}\text{FeAs}$ sample is shown in fig. 4. It is noteworthy that T_c increases as the pressure increases from ambient pressure to 3 GPa, followed by a quick decrease at higher pressure. The maximum T_c of 31 K is observed at about 3 GPa. The effect of pressure on T_c for $\text{Na}_{1-x}\text{FeAs}$ is compared with other iron arsenide superconductors as

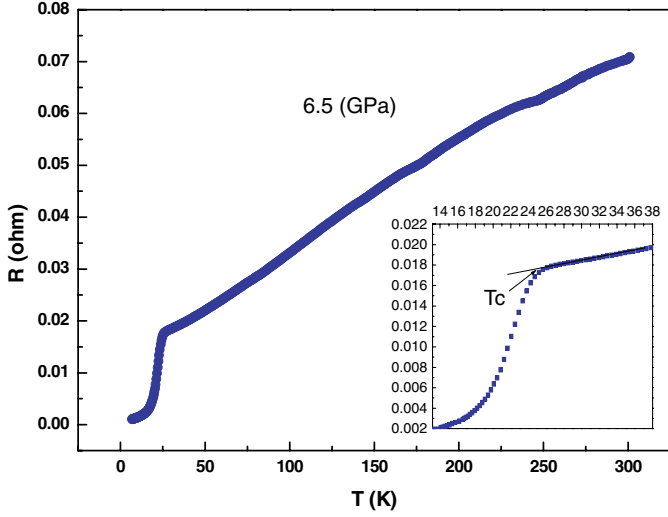


Fig. 3: (Color online) The R - T curve at 6.5 GPa. The insert shows the definition of T_c : the extrapolated line is drawn through the resistivity curve in the normal state just above T_c . The T_c is determined from the initial deviation from this line.

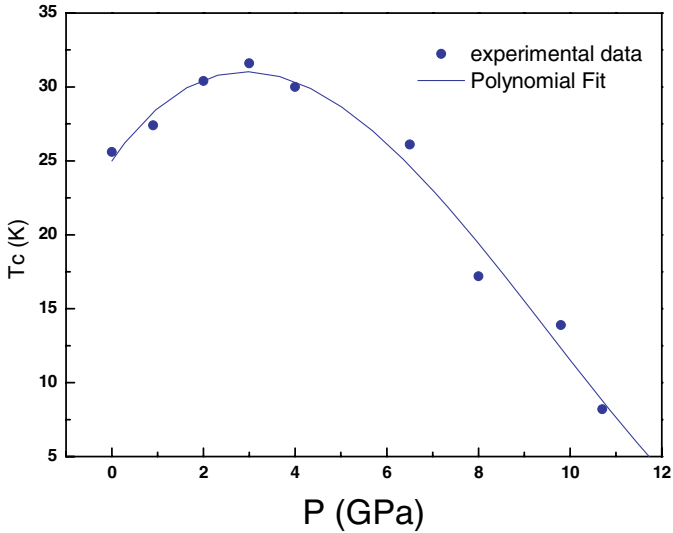


Fig. 4: (Color online) The T_c - P phase diagram of $\text{Na}_{1-x}\text{FeAs}$ obtained from resistance measurements. Points are experimental data, while the lines are polynomial fit to the experimental data.

shown in fig. 5. Two types of behaviors of the superconducting transition evolution with pressure are observed in these iron arsenide superconductors. For the first type, the T_c is enhanced or induced by initial compression, and then decreases at higher pressure. This behavior is observed in $\text{LaFeAsO}_{1-x}\text{F}_x$ [14,15], AFe_2As_2 ($A = \text{Sr}, \text{Ba}$) [16,17] and $\text{Na}_{1-x}\text{FeAs}$ in the present work. For the second type the T_c is suppressed by the applied pressure. This is observed in Li_xFeAs [20–22] or in REFeAsO_{1-x} where RE stands for rare-earth elements with smaller ion radius than La [18,19].

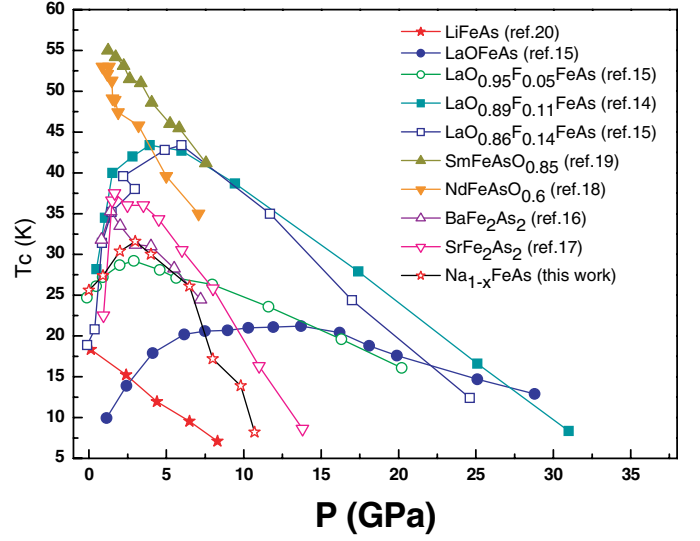


Fig. 5: (Color online) The comparison of T_c - P phase diagrams of iron arsenide superconductors. All points are experimental data with reference indicated.

Crystal chemistry parameters such as bond distance or bond angle are critical to superconducting transition temperatures for the iron arsenide superconductors. Our primary experiments of high-pressure synchrotron X-ray diffractions indicate that $\text{Na}_{1-x}\text{FeAs}$ keeps stable at least up to 20 GPa. Therefore the superconductivity evolution observed in the present work is merely caused by the changes of electronic structure at high pressure. There are two ways to generate or initiate superconductivity in iron-based superconducting systems: chemical doping or applied pressure. Both of them can result in the change of electronic structure through inducing carriers into $[\text{FeAs}]$ layers. Here the FeAs_4 tetrahedron geometry is considered crucial to determine the superconducting transition temperature. According to the experimental results in ref. [26], the ideal As–Fe–As bond angle of $\alpha = \beta = 109.47^\circ$ corresponds to the highest T_c of the “1111” system. The results suggest that the change of T_c with chemical doping is much related to the structural distortion from the ideal FeAs_4 tetrahedron. Furthermore, the high-pressure angle-dispersive X-ray diffraction experiments on $\text{NdO}_{0.88}\text{F}_{0.12}\text{FeAs}$ show that the As–Fe–As bond angles gradually deviate from ideal tetrahedron values with applied pressure [27]. It is consistent with the experimental result that the T_c is suppressed with compression in NdFeAsO_{1-x} . Not only the deviation of As–Fe–As bond angle from the ideal FeAs_4 tetrahedron results in the change of density of states (DOS) at the Fermi surface, but also the decreasing Fe–Fe distance will broaden the energy band width that usually gives rise to the decrease of its DOS at the Fermi surface. It is also confirmed by calculations that the tuning Fe–As distance modifies both the DOS near the Fermi level and the magnetic moment [28]. Therefore the change of intraplanar Fe–Fe

distance, Fe-As distance and FeAs₄ tetrahedron distortion with pressure will work together leading to the evolution of the superconducting transition temperature. Furthermore systematic synchrotron X-ray diffraction experiments for Na_{1-x}FeAs at high pressure are needed in order to get quantitative understanding about the chemical bonding length or angle based on Rietveld refinements.

In summary, the superconducting transition temperature of “111”-type Na_{1-x}FeAs was enhanced to 31 K at 3 GPa, reaching the record high T_c in the “111” system. The pressure effects on T_c for isostructural Li_xFeAs and Na_{1-x}FeAs are different: pressure suppresses T_c for Li_xFeAs, while it enhances T_c for Na_{1-x}FeAs. This is assumed to be related with the pressure-tuned geometric evolution.

This work was partially supported by NSF & MOST of China through research projects. The work involving Los Alamos National Laboratory was supported by LANL/LDRD program and LANL is operated by Los Alamos National Security LLC under DOE contract DEAC52-06NA25396. HPCAT is supported by DOE-BES, DOE-NNSA, NSF.

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