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### Superconductivity at 31 K in the "111"-type iron arsenide superconductor $Na_{1-x}$ FeAs induced by pressure

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**Abstract** – The effect of pressure on the superconductivity of "111"-type Na<sub>1-x</sub>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 Na<sub>1-x</sub>FeAs is much different from that in Li<sub>x</sub>FeAs, although they have the same Cu<sub>2</sub>Sb-type structure.

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Introduction. - The discovery of superconductivity at 26 K in  $LaO_{1-x}F_xFeAs$  [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 = rareearth), the "122"-type BaFe<sub>2</sub>As<sub>2</sub> with a tetragonal ThCr<sub>2</sub>Si<sub>2</sub>-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  $Na_{1-x}$  FeAs was also found to be superconducting with  $T_c = 9-26 \text{ K} [9-11]$  at ambient pressure. Different from the "1111"-type or "122"-type compounds, the spin density wave (SDW) transition seems absent in  $Li_x$ FeAs, 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  $LaO_{1-x}F_xFeAs$ [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<sub>2</sub>As<sub>2</sub> (A = Sr, Ba) [16,17]. For doped REFeAsO<sub>1-x</sub> 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  $\text{Li}_x$  FeAs [20–22]. More recently,  $\alpha$ -FeSe, with a structure composed of anti-PbO-type FeSe layers, was found to exhibit superconductivity at about 8K 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 Na<sub>1-x</sub>FeAs. The results are compared with those for the isostructural superconductor  $\text{Li}_x$ FeAs.

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**Experimental details.** – The  $Na_{1-x}$  FeAs compound used in the experiment was synthesized by the solidstate reaction method using Na<sub>3</sub>As, Fe and As as starting materials following the method described in ref. [8]. Considering volatility loss of Na in the sintering process, the Na<sub>3</sub>As precursor powder, Fe and As powder were mixed according to mole ratio of Na: Fe: As = 1.2:1:1that 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  $0.02^{\circ}$  and  $15 \, \text{s/step}$ . The composition of the sample was analyzed using an inductively coupled plasma (ICP) spectrometer. The results were Na: Fe: 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  $Na_{1-x}$ 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  $250\,\mu\mathrm{m}$  to  $\sim 40\,\mu\mathrm{m}$  thickness before drilling a  $250\,\mu\mathrm{m}$  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  $18\,\mu\mathrm{m}$  diameter were used as electrode leads. The  $Na_{1-x}$ 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  $Na_{1-x}$  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 Na<sub>1-x</sub>FeAs sample can be indexed by the Cu<sub>2</sub>Sb-type structure with P4/nmm symmetry, as shown in fig. 1, isostructural with Li<sub>x</sub>FeAs [8]. Figure 2 shows the electric resistance of Na<sub>1-x</sub>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 Na<sub>1-x</sub>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  $Na_{1.2}$ FeAs. The  $Na_{1-x}$ FeAs crystallizes into the Cu<sub>2</sub>Sb-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  $Na_{1-x}$  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-Tcurve as shown in fig. 3. The pressure dependence of  $T_c$ of the Na<sub>1-x</sub>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 Na<sub>1-x</sub>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 Na<sub>1-x</sub>FeAs obtained from resistance measurements. Points are experimental data, while the lines are polynominal 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 LaFeAsO<sub>1-x</sub>F<sub>x</sub> [14,15], AFe<sub>2</sub>As<sub>2</sub> (A = Sr, Ba) [16,17] and Na<sub>1-x</sub>FeAs in the present work. For the second type the  $T_c$  is suppressed by the applied pressure. This is observed in Li<sub>x</sub>FeAs [20-22] or in REFeAsO<sub>1-x</sub> 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  $Na_{1-x}$  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 [FeAs] layers. Here the FeAs<sub>4</sub> 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 highpressure angle-dispersive X-ray diffraction experiments on NdO<sub>0.88</sub>F<sub>0.12</sub>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<sub>1-x</sub>. Not only the deviation of As–Fe–As bond angle from the ideal FeAs<sub>4</sub> 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 FeAs<sub>4</sub> 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<sub>1-x</sub>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<sub>x</sub>FeAs and Na<sub>1-x</sub>FeAs are different: pressure suppresses  $T_c$  for Li<sub>x</sub>FeAs, while it enhances  $T_c$  for Na<sub>1-x</sub>FeAs. This is assumed to be related with the pressure-tuned geometric evolution.

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