Spin glass instead of superconductivity in 
$\text{Ba(Fe}_{1-x}\text{Cr}_{x/2}\text{Ni}_{x/2})_2\text{As}_2$

Sheng-Gao Xu, Yun-Lei Sun, Shuai Jiang, Hui Xing, Lin Jiao, 
Hui-Qiu Yuan, Chun-Mu Feng, Zhu-An Xu and Guang-Han Cao
Department of Physics, Zhejiang University, Hangzhou, China
E-mail: ghcao@zju.edu.cn

Abstract. We have studied an “isoelectronic” Fe-site doping with Cr and Ni in $\text{Ba(Fe}_{1-x}\text{Cr}_{x/2}\text{Ni}_{x/2})_2\text{As}_2$ system. With increasing $x$, the antiferromagnetic SDW in the parent compound is suppressed quickly. Spin glass state emerges in the range of $0.1 \leq x < 0.2$. The spin glass state evolves into cluster glass with further doping, and finally becomes ferromagnetism at $x = 1.0$. No superconductivity was observed down to 0.5 K. The electronic phase diagram is established, and the underlying physics is discussed.

1. Introduction
Most Fe-based superconductors have a parent compound whose ground state is antiferromagnetic (AFM) spin-density wave (SDW). Superconductivity (SC) emerges as the SDW order is suppressed by either chemical doping or applying pressures.[1] For instance, $\text{BaFe}_2\text{As}_2$ undergoes an SDW transition at 138 K.[2, 3] SC was realized by the hole doping with K[4], and electron doping with Co[5] or Ni[6]. Interestingly, an isoelectronic doping at As-site with P[7] or at Fe-site with Ru[8] similarly induces SC. These results seem to suggest that SC will definitely appear if the SDW order is destroyed. In this paper, we try to check this point by a co-doping study. We employed equal amount of Ni and Cr to substitute for Fe for reasons below. First, Ni (Cr) has two more (less) 3d electrons than Fe has, and the Ni/Cr doping keeps the number of 3d electrons unchanged, namely it is an isoelectronic doping. Secondly Fe, Ni and Cr are all 3d elements, so that chemical pressure effect is negligible. Thirdly the solubility of Ni and Cr is very high, which is beneficial to have an extended survey.

We previously found that small amount of Ni doping in $\text{BaFe}_2\text{As}_2$ greatly suppresses the SDW ordering, and superconducting transition at $T_c=20.5$ K appears at the doping level of 5 %.[6] The result was later reproduced and detailed phase diagram was established.[9] On the other hand, the Cr doping also suppresses the SDW ordering, though much mildly.[10] Therefore, how the simultaneous doping with Ni and Cr would influence the SDW order, and whether it induces SC, are of great interest.

2. Experimental
Polycrystalline samples of $\text{Ba(Fe}_{1-x}\text{Cr}_{x/2}\text{Ni}_{x/2})_2\text{As}_2$ ($x=0, 0.06, 0.08, 0.10, 0.12, 0.20, 0.30, 0.50, 0.75$ and $1.0$) were prepared by solid state reaction with stoichiometric amount of the elements Ba, Fe, Cr, Ni and As (purity higher than 99.9%). The mixture was placed in alumina tubes,
sealed in an evacuated quartz tube, and then heated to 1023 K holding for 20 h. After cooling down, the intermediate product was ground thoroughly, then pressed into pellets. The pellets were allowed to react again at 1123 K for 24 h in vacuum. The experiment was mostly performed in an argon-filled glove-box to avoid any moisture and oxidation.

Powder x-ray diffraction (XRD) was carried out at room temperature using a D/Max-rA diffractometer with Cu-Kα radiations and a graphite monochromator. Lattice parameters were refined by a least-squares fit with considerations of zero shift. The electrical resistivity was measured using a standard four-probe method. The dc magnetization was measured in the zero-field cooling (ZFC) and field cooling (FC) modes on a Quantum Design Magnetic Property Measurement System (MPMS-5). The ac magnetization was measured on a Quantum Design Physical Property Measurement System (PPMS-9).

3. Results and discussion

The XRD patterns of the as-prepared Ba(Fe$_{1-x}$Cr$_{x/2}$Ni$_{x/2}$)As$_2$ are shown in Fig. 1(a). Only small amount of impurity is seen for a few samples. As expected, the system crystallizes in tetragonal ThCr$_2$Si$_2$-type structure with space group I4/mmm. The fitted lattice parameters [Fig. 1(b)] indicate that the a-axis increases gradually, but the c-axis tends to decrease, with the Ni/Cr doping. The systematic change in cell constants indicates that the Ni and Cr indeed incorporates the lattice.

Figure 2 shows the temperature dependence of resistivity of Ba(Fe$_{1-x}$Cr$_{x/2}$Ni$_{x/2}$)As$_2$. The parent compound BaFe$_2$As$_2$ exhibits a drop in resistivity at 140 K, consistent with the previous report.[2] The resistivity anomaly is due to an AFM SDW transition.[3] Upon the Ni/Cr doping, the SDW transition temperature $T_{SDW}$ decreases gradually. However, it is not as quickly as the Ni-doping does. This may be due to the "neutralization" by the simultaneous Cr doping. Although the resistivity anomaly is almost completely suppressed at $x=0.12$, we did not observe SC above 0.5 K for $0.06 \leq x \leq 0.12$. For $x=0.3$ through 0.5, the resistivity varies little in decreasing temperatures from 300 K down to 3 K. Unexpectedly, the sample of $x=0.75$ shows semiconducting behaviour, which could be related with the novel c-axis shown in Fig. 1(b). For $x=1.0$, the resistivity shows an obvious kink at 64 K, which is due to a ferromagnetic transition (see below).

Fig. 3 shows the temperature dependence of dc magnetization for Ba(Fe$_{1-x}$Cr$_{x/2}$Ni$_{x/2}$)As$_2$. 

Figure 1. (a) Powder X-ray diffraction patterns of Ba(Fe$_{1-x}$Cr$_{x/2}$Ni$_{x/2}$)As$_2$ polycrystalline samples at room temperature. The peaks marked by asterisks come from small amount of impurities. (b) Fitted lattice parameters plotted as functions of doping $x$. 

26th International Conference on Low Temperature Physics (LT26) IOP Publishing
Journal of Physics: Conference Series 400 (2012) 032115
doi:10.1088/1742-6596/400/3/032115
Figure 2. Temperature dependence of resistivity for Ba(Fe\textsubscript{1-x}Cr\textsubscript{x}/2Ni\textsubscript{x}/2)\textsubscript{As} polycrystalline samples. The arrows mark the positions of the related transition temperatures. The insets give an expanded view for some data.

Figure 3. Temperature dependence of dc magnetization for Ba(Fe\textsubscript{1-x}Cr\textsubscript{x}/2Ni\textsubscript{x}/2)\textsubscript{As} with x=0.06 to 0.3. The frequency f in the ZFC curves separate. This phenomenon is the typical behaviour of spin glass state. With further increasing x up to 0.75, the magnetization at the peak of M\textsubscript{ZFC} is over one order of magnitude higher, suggesting a cluster-glass state below the T\textsubscript{f}. The frequency dependence of ac magnetization confirms the magnetic state of spin glass and/or cluster glass (not shown here).

For the samples of x=0.06 and 0.08, evidence of SDW transition can also be identified at 55 K and 35 K (marked by arrows), respectively, although the data suggest the existence of small amount of magnetic impurities. The samples of x=0.1 and 0.12 show a peak at T\textsubscript{f} in the ZFC data, where the M\textsubscript{FC} and M\textsubscript{ZFC} curves separate. This phenomenon is the typical behaviour of spin glass state. With further increasing x up to 0.75, the magnetization at the peak of M\textsubscript{ZFC} is over one order of magnitude higher, suggesting a cluster-glass state below the T\textsubscript{f}. The frequency dependence of ac magnetization confirms the magnetic state of spin glass and/or cluster glass (not shown here).

Interestingly, ferromagnetism emerges when the iron is completely replaced by Ni/Cr, as shown in Fig. 4. The Curie temperature is 64 K where the magnetization increases abruptly with decreasing temperature. Above the Curie point, the magnetic susceptibility follows the Curie-Weiss law. The large bifurcation between M\textsubscript{FC} and M\textsubscript{ZFC} under a field of 1000 Oe...
suggests high coercive fields. Indeed, we observed a coercive field as high as 10000 Oe at 2 K. The saturated magnetization is about 0.5 $\mu_B$/f.u., suggesting an itinerant ferromagnetism.

Figure 4. Temperature dependence of magnetization for BaCrNiAs$_2$. The applied field is 1000 Oe.

Figure 5. Magnetic phase diagram of Ba(Fe$_{1-x}$Cr$_x$/2Ni$_x$/2)As$_2$. SDW: spin-density wave, SG: spin glass, CG: cluster glass, FM: ferromagnetism.

Based on the above data, the magnetic phase diagram is summarized in Fig. 5. The Ni/Cr doping severely suppresses the SDW ordering. At the disappearance of SDW, spin glass serves as the ground state. This is in sharp contrast with the Ni-doping case in which superconductivity emerges. With further doping, there is a crossover from spin glass to cluster glass. An itinerant ferromagnetism state emerges when the iron is completely substituted.

The formation of spin glass can be understood by the frustrated magnetic exchange interactions.[11] There are nearest neighbor ($J_1$), next nearest neighbor ($J_2$) and even long-range interactions ($J_n$) within the transition-metal planes. Basically, depending on different circumstances, the exchange interactions can be either ferromagnetic or antiferromagnetic, which could favor spin glass, cluster glass and/or ferromagnetism. The appearance of spin glass and cluster glass instead of superconductivity in Ba(Fe$_{1-x}$Cr$_x$/2Ni$_x$/2)As$_2$ system strongly suggests that the prerequisite of Fe-based superconductivity is more than the suppression of the SDW order.

Acknowledgments
This work is supported by the NSF of China (No. 10934005), National Basic Research Program of China (No. 2010CB923003).

References
[1] Johnston D C 2010 Adv. Phys. 59 803
[2] Rotter M et al 2008 Phys. Rev. B 78 020503(R)
[3] Bao W et al 2009 Phys. Rev. Lett. 102 247001
[4] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[5] Sefat A S et al 2008 Phys. Rev. Lett. 101 117004
[6] Li L J et al 2009 New J. Phys. 11 025008
[7] Jiang S et al 2009 J. Phys. Condens. Matter 21 382203
[8] Sharma S et al 2010 Phys. Rev. B 81 174512
[9] Ni N 2010 Phys. Rev. B 82 024519
[10] Sefat A S et al 2009 Phys. Rev. B 79 224524
[11] Binder K and Young A P 1986 Rev. Mod. Phys. 58 801