Effects of vanadium doping on BaFe$_2$As$_2$

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Abstract – We report an investigation of the structural, magnetic and electronic properties of Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$ using x-ray, transport, magnetic susceptibility and neutron scattering measurements. The vanadium substitutions in Fe sites are possible up to $\sim$40%. Hall effect measurements indicate strong hole-doping effect through V doping, while no superconductivity is observed in all samples down to 2 K. The antiferromagnetic and structural transition temperature of BaFe$_2$As$_2$ is gradually suppressed to finite temperature, then vanishes at $x = 0.245$ with the emergence of spin glass behavior, suggesting an avoided quantum critical point (QCP). Our results demonstrate that the avoided QCP and spin glass state which were previously reported in the superconducting phase of Co/Ni-doped BaFe$_2$As$_2$ can also be realized in non-superconducting Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$.

Introduction. – In both cuprate and Fe-based high-$T_c$ superconductors, investigation of the interplay between the magnetism and superconductivity through chemical doping is critical to explore the superconducting mechanism [1,2]. In the iron-pnictides phase diagram, besides superconductivity and antiferromagnetic (AFM) phase, various exotic states including incommensurate short-range AFM order, G-type AFM order, C$_4$ magnetic phase and spin glass state were observed, which reveals the rich physics controlled by the interplay between the spin, charge and orbital degrees of freedom in this system [3–11].

For the well-known FeAs-122 parent compound BaFe$_2$As$_2$, either electron doping (e.g., Co, Ni, Cu, Rh, Ir, Pt, Pd) [12–15] or isoelectronic doping (e.g., Ru, P) [16,17] in the FeAs plane could easily instigate superconductivity. On the hole doping side, although alkali metal doping in the Ba site could induce superconductivity with transition temperature as high as 38 K [18], attempts of hole doping in the FeAs plane (e.g., Mn, Cr, Mo) [5,7,19] show that the stripe AFM and structural transitions are suppressed to some extent but superconductivity was never observed. This contrasting behavior has not been well understood. Furthermore, the discovery of a novel C$_4$ magnetic phase only in the hole-doped 122 materials has drawn a lot of research interest [9]. Therefore, more investigations are needed for the hole doping cases in the FeAs plane.

In this paper we report the effect of V doping on BaFe$_2$As$_2$ in a bulk property and neutron/x-ray diffraction study. The Hall effect measurements indicate that V substitution for Fe results in hole doping. Although superconductivity is not observed in Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$ as in other in-plane hole-doping cases, an avoided quantum critical point with the emergence of a spin glass state is found in heavily doped samples.

Experiment. – Single crystals of Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$ were grown by the FeAs/VAs self-flux method similar to Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [20]. Polycrystalline samples were synthesized by heating stoichiometric barium, FeAs and VAs in an evacuated quartz tube at 1223 K for 30 h. The products were reground and annealed at the same temperature twice to ensure the phase purity. The elemental doping composition was measured by energy dispersive x-ray spectroscopy (EDS, Oxford X-Max 50). X-ray diffraction (XRD) patterns of powder and single crystals were collected from a Bruker D8 Advance x-ray diffractometer using Cu $K_\alpha$ radiation. Resistivity measurements were performed on a Quantum Design physical property measurement system (QD PPMS-14T).

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Table 1: Chemical composition analysis of Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$.

| Sample type     | Nominal $x$ | EDS $x$ |
|-----------------|-------------|---------|
| Single crystal  | 0.06        | 0.016   |
| Single crystal  | 0.1         | 0.031   |
| Single crystal  | 0.14        | 0.051   |
| Single crystal  | 0.20        | 0.081   |
| Single crystal  | 0.30        | 0.130   |
| Single crystal  | 0.40        | 0.183   |
| Polycrystalline| 0.26        | 0.198   |
| Polycrystalline| 0.29        | 0.221   |
| Polycrystalline| 0.30        | 0.245   |
| Polycrystalline| 0.40        | 0.315   |
| Polycrystalline| 0.50        | 0.397   |

Fig. 1: (Colour online) Room temperature lattice parameters as a function of the V-doping value $x$ determined from EDS for Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$.

Magnetization measurement was carried out in Quantum Design MPMS3. Elastic neutron scattering measurements were performed using the HB1A triple-axis spectrometer at HFIR with incident energy $E_i = 1.465$ meV and collimation of 40'-40'-40'-80'.

Results and discussion. – Single crystals with centimeter or millimeter size are obtained through the self-flux crystal growth method up to nominal doping $x = 40\%$. It is not possible to grow samples in single-crystal form at a higher doping level. However, polycrystalline samples of Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$ with nominal doping up to $x = 50\%$ can be synthesized with only a small amount of impurity phases (impurity phases including VAs are estimated to be lower than 5% from x-ray diffraction refinement). We characterized all samples with EDS and the results are listed in table 1. Figure 1 plots the lattice parameters as a function of V concentration. The $c$-lattice parameter increases monotonically with increasing $x$ which is the typical feature in hole-doped iron-pnictides material [21]. Comparing with other hole-doping cases (Mn, Cr, Mo or K) [21,22], vanadium substitution effectively expands the $c$-axis, the parameter increases by 4% at $x = 0.397$. On the other hand, there is a slight contraction for the $a$-axis lattice parameter which decreases by 0.5% at $x = 0.397$.

Magnetization results for Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$ ($0 \leq x \leq 0.183$) single crystals are presented in fig. 2(a). The data were measured in zero-field-cooling (ZFC) with magnetic field of 1 T applied parallel to the $ab$-plane and normalized by the susceptibility at 300 K. For BaFe$_2$As$_2$, the susceptibility decreases linearly with decreasing temperature, then drops abruptly below the AFM transition with $T_N \approx 133$ K. With V doping, the susceptibility increases with decreasing temperature and approaches a Curie-Weiss–like behavior. The AFM transition remains sharp in all doped single crystals. Figure 2(b) shows both the ZFC and FC magnetization results for polycrystalline samples at higher doping levels ($0.198 \leq x \leq 0.397$). For $x = 0.198$ and $x = 0.221$, the weak AFM transitions in the magnetic susceptibility are evident from the $dM/dT$ curves with $T_N \approx 43$ K and 37 K, respectively (inset of fig. 2(b)). For $x = 0.245$, no sign of magnetic transition can be inferred from the $M$-$T$ curve, while the separation between ZFC and FC susceptibilities at low temperatures indicates a spin glass behavior (SG). Such behavior
are new AFM-like kinks (marked as T*) in the M-T curves at around 20 K, indicating possible new short-range AFM fluctuations. In addition, we calculated the paramagnetic moments from the Curie-Weiss fit of susceptibility data for heavily V-doped samples (x = 0.315 and x = 0.397). Assuming that the whole moment contribution is from V, the results show that the average moment brought by one V ion is about 2.9μB, which is quite close to the theoretical moment value of one free V³⁺ ion.

Figure 3 presents the normalized electrical transport data ρ/ρ₀ₓ₀K. The temperature-dependent resistivity for BaFe₂As₂ shows a sharp drop anomaly at the AFM/structural transition, while for the V-doped samples the feature becomes a sharp upturn and gradually moves to lower temperatures with increasing x. The temperatures of resistivity anomalies determined from the minimum of dρ/dT are consistent with the Tₙ from the M-T curves. At x = 0.198 and x = 0.221, the weak features of resistivity anomalies are still visible from the dρ/dT curves as shown in the inset of fig. 3(b). However, from x ≥ 0.245, such anomaly could not be detected anymore, indicating the absence of AFM/structural transition. Furthermore, the resistivity increases approximately logarithmically with decreasing temperature below 50 K as shown in the right inset of fig. 3(b), which is a characteristic of Kondo scattering. This behavior suggests that the vanadium dopants act as magnetic impurities.

The Hall coefficients R_H at different temperatures for Ba(Fe₁₋ₓVₓ)₂As₂ (0 ≤ x ≤ 0.13) single crystals are presented in fig. 4. R_H changes suddenly from a negative value in the undoped sample to a positive one with slight V doping at low temperatures, and becomes completely positive in the whole temperature region measured at x = 0.051. Comparing to the Hall effect in Cr doping [5], the sign reversal of R_H initially increases, then decreases at x = 0.130. This feature is quite similar to the Hall effect in Ba₀.₆K₀.₄Fe₂As₂ [23], which is explained as the result of asymmetric scattering between the electron and hole bands where the mobility is much larger for the former [20,23].

Neutron diffraction experiments were performed on single crystals at x = 0.031, 0.051 and 0.130, the results are shown in fig. 5(a)–(c). The AFM transition was characterized by measuring the temperature dependence of (0.5 0.5 1)τ magnetic Bragg peak and the tetragonal-to-orthorhombic structural transition is identified by the intensity change of the (1 1 2)τ nuclear peak (T refers to the tetragonal basis) [24]. Combining the neutron scattering data and resistivity results of dρ/dT, where only one transition anomaly is observed, both the structural and magnetic transitions occur at the same temperature for V-doped samples. This agrees with other hole-doped FeAs-122 cases (Cr, Mn, Mo and K) [6,7,19,25], but different from the electron-doping cases in which Tₙ and Tₘ are well separated [26]. The doping dependence of the refined magnetic moment is presented in fig. 5(d). For the electron-doping cases such as Co-doped BaFe₂As₂, the ordered moment is linearly suppressed with doping and finally becomes zero with 5% Co doping [27]. For the hole-doping cases like Ba(Fe₁₋ₓCrₓ)₂As₂, the magnetic moment is independent of concentration for x ≤ 0.2.
Despite suppression of the transition temperature from 133 K to 56 K. Then the moment quickly decreases to about 0.3μB at x = 0.335 [6]. While for the V-doping case, the moment evolution seems to be slightly different. The average ordered Fe/V moment first decreases in the range of 0 ≤ x ≤ 0.051, then becomes almost doping independent from x = 0.051 (0.62μB) to x = 0.13 (0.64μB).

Based on the experimental results above, the T-x phase diagram for V-doped BaFe2As2 is presented in fig. 6. There is a gradual suppression of the AFM/structural transition temperature of BaFe2As2 from 133 K to 37 K with increasing x. The decreasing of AFM transition temperature actually follows a linear behavior with increasing c, see the inset of fig. 6. Usually one would expect a doping-induced magnetic quantum critical point. However, the AFM/structural transition suddenly vanishes at x = 0.245 and c = 13.54 Å. On the other hand, a spin glass state is detected on the vanishing point of AFM order. These observations strongly suggest an avoided quantum critical point (QCP) by the development of competing states [26,28]. Magnetic QCP should not be a necessary condition for Fe-based superconductivity, it is interesting to mention that for Co- or Ni-doped BaFe2As2, near the optimal doping with maximum Tc, there were also reports about an avoided QCP [26] and clustered spin glass state [10,11]. The spin glass in BaFe2−x(Co/Ni)xAs2 was previously interpreted as an intrinsic response to the competition between the superconductivity and antiferromagnetism [10], but a similar explanation is not applicable for the SG in Ba(Fe1−xV)x2As2 since no superconductivity was observed for the V-doped samples. The most plausible explanation is that the magnetic impurity V in metallic hosts could result in the Ruderman-Kittel-Kasuya-Yosida (RKKY) effective exchange interaction between the impurity spins, which leads to a spin glass behavior [29,30].

The AFM-like kinks (T*) observed in the M-T curves at x = 0.315, 0.397 closely resemble the behavior of the checkerboard (G-type) AFM order in Cr- and Mn-doped BaFe2As2 [6,7]. According to calculations in Mn-doped BaFe2As2, the doped magnetic impurities would exhibit a G-type magnetic structure close to their cores in a heavily doped region when the RKKY interactions between the conducting electrons and the magnetic impurities are taken into account [29]. Similarly, the T* in the V-doped samples most probably represents the formation of short-range local G-type AFM fluctuations. The Fe-based superconductivity may be accompanied by the spin fluctuations of the 3d electrons of Fe which are possibly suppressed by the competition of G-type spin fluctuations brought by V.

**Conclusion.** – As a magnetic impurity, the doping of V into BaFe2As2 suppresses the AFM order and generates an effective hole-doping effect, no superconductivity is observed which is in contrast with the K-doped BaFe2As2. This indicates the extreme sensitivity of the in-plane magnetic impurity for Fe-based superconductivity. On the other hand, the RKKY spin glass behavior accompanied by possible checkerboard antiferromagnetic fluctuations emerges at higher doping levels. The phase
diagram of Ba(Fe$_{1-x}$V$_x$)$_2$As$_2$ exhibits an avoided QCP similar to that in Ni-doped BaFe$_2$As$_2$.

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