Superconductivity

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Superconductivity and Crystal Structures of $(Ba_{1-x}K_x)Fe_2As_2$ ($x = 0$–1)**

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The discovery of iron arsenide superconductors has opened new avenues for superconductivity research. Initial reports on the critical temperatures (T_c) for $LaFeAs(O_{1-x}F_x)$ of 26–43 K[1,2] were quickly followed by even higher transition temperatures, up to 55 K in $SmFeAs(O_{1-x}F_x)$.[3] It is accepted that iron arsenides represent a further class of high-T_c superconductors,[4] 22 years after the discovery of the cuprates.[5]

Similar to the cuprates, superconductivity in iron arsenides emerges from two-dimensional, antiferromagnetically ordered layers in the parent compound. LaFeAsO crystallizes in the ZrCuSiAs-type structure,[6] composed of alternating $(LaO)^+$ and $(FeAs)^-$ layers (Figure 1, left). Superconductivity is induced by partial oxidation (hole doping)[7] or reduction (electron doping) of the $(FeAs)^{\delta-}$ layers. Electron doping, by substitution of oxide for fluoride or by oxide vacancies, has been highly successful, whereas only one case of hole-doped LaFeAsO has been reported to date.[8]

Recently, we proposed the ternary iron arsenide $BaFe_2As_2$[9] with the $ThCr_2Si_2$-type structure as a potential new parent compound.[10] Our idea was based on the very similar structural and electronic conditions of this ternary arsenide in comparison to LaFeAsO. $BaFe_2As_2$ and LaFeAsO contain identical (FeAs) layers, which also have the same charge in accordance with $Ba^{2+}[(FeAs)^-]_2$. Figure 1 shows both structures. Partial replacement of barium for potassium (hole doping) induced superconductivity at 38 K in $(Ba_{0.6}K_{0.4})Fe_2As_2$,[11] the first member of a new family of superconducting iron arsenides. Our discovery was quickly followed by reports of similar compounds with strontium ($T_c \approx 37$ K),[12,13] calcium ($T_c \approx 20$ K),[14] and europium ($T_c = 32$ K).[15] Since then, research on superconducting iron arsenides has largely focused on ternary compounds with the $ThCr_2Si_2$-type structure, rather than arsenide oxides (LaFeAsO derivatives). This is because single-phase samples and also large single crystals of the ternary compounds are much easier to obtain.

Even though several findings suggest unconventional (non-BCS) superconductivity in iron arsenides,[16–18] the pairing mechanism is unclear.[19] A generally accepted key aspect for both LaFeAsO and $BaFe_2As_2$ families is a magnetic and structural phase transition in the undoped phases, occurring at temperatures between 140–203 K.[10,20–22] In the course of this transition, the tetragonal symmetry of the $ThCr_2Si_2$-type structure (space group $I4/mmm$) turns into the orthorhombic β-$SrRh_2As_2$-type[23] (space group $Fmmm$) before antiferromagnetic spin-ordering emerges. Recently, we have elucidated the spin structure of $BaFe_2As_2$ by single-crystal neutron diffraction.[24]

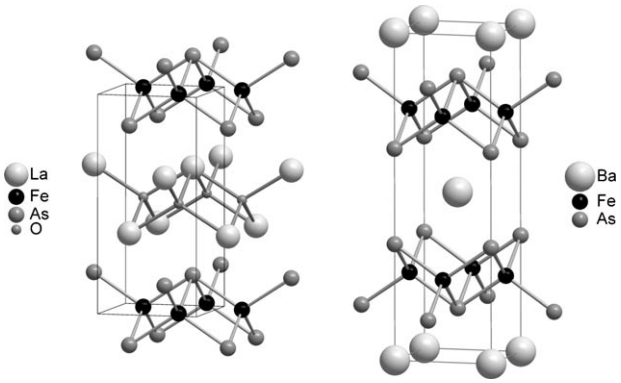

Figure 1. Crystal structures of LaFeAsO (left) and $BaFe_2As_2$ (right).

It had been believed that the magnetic and structural phase transitions of LaFeAsO and $BaFe_2As_2$ has to be suppressed by doping, so that superconductivity can emerge. But recently it was reported, that superconductivity up to 29 K occurs even in undoped AFe_2As_2 (A = Ca, Sr, Ba) under pressure.[25] Thus all the signs are that destabilization of the antiferromagnetic state either by doping or pressure is a main issue for superconductivity in iron arsenides. However, it is still debatable whether both states may coexist.

The doping dependency of the structure and superconductivity has been intensively studied on LaFeAsO-type compounds. In electron-doped $REFeAsO_{1-x}$ (RE = La–Sm),[26] T_c increases with higher doping levels and with decreasing lattice parameters. Conversely, the hole-doped system $(La_{1-x}Sr_x)FeAsO$[27] also shows increasing T_c with higher doping levels, but with concurrently increasing lattice parameters. This indicates that the doping level is the determining parameter for T_c in LaFeAsO compounds. However, these results are limited by the fact that the exact oxygen or fluorine content in doped LaFeAsO compounds is unknown in most cases and, furthermore, doping levels over $x \approx 0.2$ have not been achieved. Moreover, the changes in the lattice parameters are very small and their significance is often doubtful.

In contrast, the potassium-doped $BaFe_2As_2$ system provides a good opportunity for doping studies. KFe_2As_2 is a known compound,[28] indicating that K-doping of $BaFe_2As_2$ should be feasible owing to the similar ionic radii of Ba^{2+} (1.42 Å) and K^+ (1.51 Å).[29] To date, we have only reported

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the occurrence of superconductivity in $(Ba_{0.6}K_{0.4})Fe_2As_2$, whereas the dependencies of superconductivity and crystal structures on the potassium content in the whole solid solution $(Ba_{1-x}K_x)Fe_2As_2$ are still unknown. Herein, we report on the synthesis, crystal structures, and superconducting transition temperatures of the complete series $(Ba_{1-x}K_x)Fe_2As_2$ ($x = 0$–1).

The ternary compounds $BaFe_2As_2$ and KFe_2As_2 both adopt a pronounced two-dimensional form of the $ThCr_2Si_2$-type structure, without As–As bonds between the layers. The unit cells have approximately equal volumes, despite the slightly greater ionic radius of K^+. On the other hand, the ratios of lattice parameters (c/a) differ considerably, as the c lattice parameter of KFe_2As_2 is almost 1 Å longer than that of $BaFe_2As_2$. In other words, the unit cell of KFe_2As_2 is elongated along the c axis.

The crystal structures of the compounds $(Ba_{1-x}K_x)Fe_2As_2$ were determined by Rietveld refinements of X-ray powder patterns as shown in Figure 2 for $(Ba_{0.9}K_{0.1})Fe_2As_2$. Figure 3

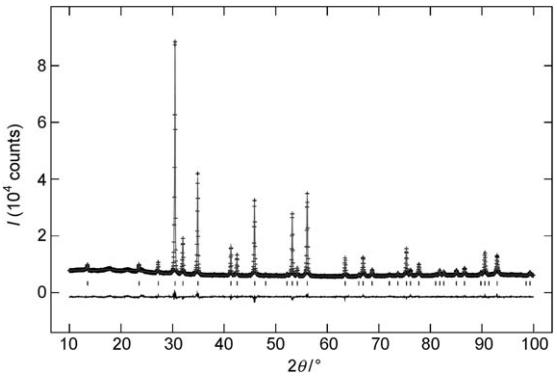

Figure 2. Measured (+) and calculated (——) X-ray powder pattern of $(Ba_{0.9}K_{0.1})Fe_2As_2$.

shows the changes of the structure with potassium doping. The lattice parameters a and c vary linearly with the potassium content over the whole range. The unit cell volume is constant within the experimental error, because the significant elongation of the c axis is almost compensated by the decrease of the a axis.[30] Also the Fe–As and Ba(K)–As bond lengths remain unchanged. Both parameters vary by less than 0.4% and are therefore not shown.

In addition to the lattice parameters, the Fe–Fe bond length and the As-Fe-As bond angle ε change significantly (by 5–7%) on doping. Both decrease linearly with increasing potassium content, which means that the $FeAs_4$ tetrahedra become more elongated along the c axis, and the iron atoms move closer together. Interestingly, ε becomes the ideal tetrahedral angle of 109.5° at $x \approx 0.4$. The structure shown in Figure 3 depicts the ε angle in the (FeAs) layer. Thus, the main effect of doping on the crystal structure of $(Ba_{1-x}K_x)Fe_2As_2$ at room temperature is a decreasing As-Fe-As bond angle and a concurrent shortening of the distances between the iron atoms.

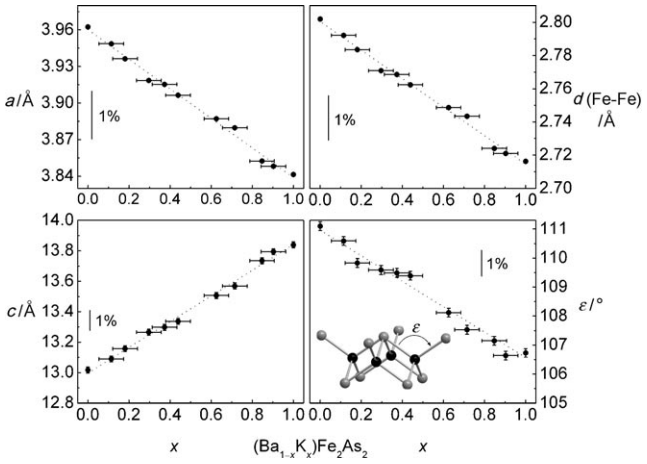

Figure 3. Variation of structural parameters in $(Ba_{1-x}K_x)Fe_2As_2$ with x.

Chemical bonding in $ThCr_2Si_2$-type compounds has been intensively studied.[31] We have shown that the properties of these compounds depend on a subtle balance between different bonding interactions, especially on the interplay between metal–ligand (Fe–As) and metal–metal (Fe–Fe) bonding within the layers.[32] In the case of $BaFe_2As_2$, it is accepted that the Fe $3d_{x^2-y^2}$-orbitals close to the Fermi level play a key role in magnetism and superconductivity. The angle ε determines the overlap between Fe $3d_{x^2-y^2}$ and As 3s,p orbitals, thus our results suggest a strong coupling of structural and electronic degrees of freedom by doping.

It is disputed whether the structural phase transition in iron arsenides has to be completely suppressed before superconductivity can occur. Recent results show that the structural distortion of LaFeAsO disappears by doping exactly at the boundary of the superconducting state.[33] In the case of $BaFe_2As_2$, we have already shown that the tetragonal to orthorhombic phase transition is suppressed in the superconductor $(Ba_{0.6}K_{0.4})Fe_2As_2$, which remains tetragonal at low temperature.[11] To delimit the composition range of the structural transition, we have measured X-ray powder diffraction patterns of $(Ba_{1-x}K_x)Fe_2As_2$ ($x = 0$–0.3) between 300 and 10 K. Figure 4 shows the temperature dependences of the (110) reflections of the tetragonal structure with decreasing temperature. The reduction of the lattice symmetry and thus the phase transition is indicated by peak splitting, at $x = 0$ and 0.1, or broadening at $x = 0.2$, but is absent at $x = 0.3$. The transition temperatures (T_{tr}) decrease strongly with higher potassium content (x value) from 140 K to approximately 90 K at $x = 0.2$, where the transition proceeds over a wide temperature range. We thus conclude that the orthorhombic phase (space group *Fmmm*) exists at low temperatures up to $x = 0.2$ and becomes first tetragonal at higher doping levels, between $x = 0.2$ and 0.3.

We have also investigated the effect of doping on superconductivity. Therefore, we measured the electrical resistances R of $(Ba_{1-x}K_x)Fe_2As_2$ samples ($x = 0$–1) between 1.8 K and 300 K by a four-probe method. The relative changes of the resistance with temperature ($R/R_{300\,K}$) of all samples are shown in Figure 5. Superconductivity was detected in all cases except for the undoped parent compound $BaFe_2As_2$, but the

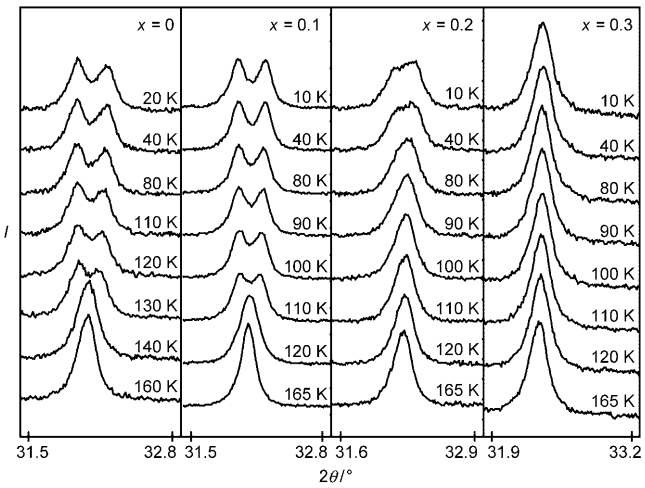

Figure 4. Temperature dependence of the (110) reflections in $(Ba_{1-x}K_x)Fe_2As_2$ with $x = 0$–0.3.

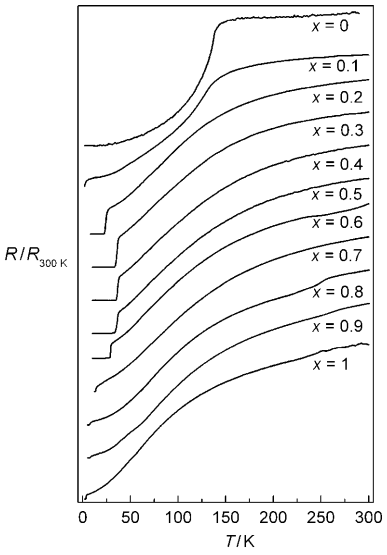

Figure 5. Relative electrical resistances (R/R_{300K}) of $(Ba_{1-x}K_x)Fe_2As_2$ samples.

transition temperatures vary strongly. $BaFe_2As_2$ has relatively poor metallic properties with a specific resistivity around 1 mΩcm at room temperature and exhibits the structural and magnetic phase transition at 140 K,[10] which is clearly visible in the resistance plot (Figure 5, top trace).

At the smallest doping level, $x \approx 0.1$, the resistance anomaly is not completely suppressed, but shifted to lower temperature. There is an abrupt drop in the resistance at approximately 3 K, which is the onset of superconductivity. However, zero resistance could not be achieved at 1.8 K, but superconductivity was verified by magnetic measurements. The anomaly in the resistance appears to be suppressed when the doping level is at $x = 0.2$ where the behavior is of a normal metal, until superconductivity is reached at $T_c \approx 25$ K. The transition temperature increases significantly to 36 K and 38 K for $x = 0.3$ and $x = 0.4$, respectively. Doping levels of $x > 0.5$ lead to a continuous decrease of T_c to 3.8 K for KFe_2As_2.

The phase diagram in Figure 6 shows the superconducting critical temperatures (T_c), as well as the phase transition temperatures (T_{tr}) for $(Ba_{1-x}K_x)Fe_2As_2$. Superconductivity is found for all compositions except the parent compound and with $T_c > 30$ K in the range $x = 0.3$–0.6 with a maximum of 38 K close to $x = 0.4$. The orthorhombically distorted crystal structure exists up to $x = 0.2$, where T_c is approximately 25 K. Thus, superconductivity apparently coexists with the distorted orthorhombic structure and potentially with the antiferromagnetic state which is known for the orthorhombic form of $BaFe_2As_2$.

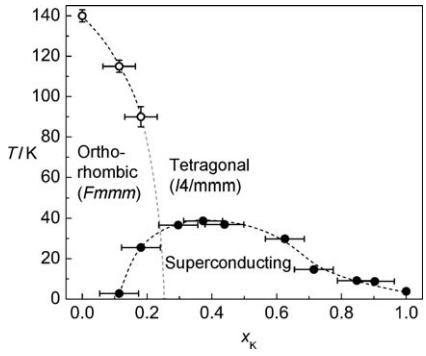

Figure 6. Phase diagram of $(Ba_{1-x}K_x)Fe_2As_2$ with the critical (●) and phase transition (○) temperatures. Dashed lines are guides for the eye.

In summary, we have shown experimental doping dependencies of the crystal structure, the phase transition, and superconductivity in the solid solution $(Ba_{1-x}K_x)Fe_2As_2$. The main effects of doping on the crystal structure at room temperature are a decrease in the As-Fe-As bond angle (ε) in the $FeAs_4$ tetrahedra and in the Fe–Fe bond length, equivalent to an elongation of the (FeAs) tetrahedra along the axis [001]. This is in contradiction to the results of recently reported density functional calculations, where the opposing effect was proposed.[34] The structural changes are intimately coupled to the electronic states at the Fermi level, because the most relevant Fe $3d_{x^2-y^2}$ orbitals are strongly affected by the bond angle ε. We have detected structural phase transitions ($I4/mmm \rightarrow Fmmm$) analogue to $BaFe_2As_2$, which have decreasing transition temperatures up to a doping level of $x = 0.2$. At higher potassium contents the structure remains tetragonal down to 10 K. Superconductivity occurs over the whole doping range from $x = 0.1$ in $(Ba_{1-x}K_x)Fe_2As_2$ with a maximum T_c of 38 K at $x \approx 0.4$. The parent compound $BaFe_2As_2$ is non-superconducting above 1.8 K. The superconducting transitions in the orthorhombic compounds $(Ba_{0.9}K_{0.1})Fe_2As_2$ ($T_c \approx 3$ K) and $(Ba_{0.8}K_{0.2})Fe_2As_2$ ($T_c \approx 25$ K) give strong evidence for the coexistence of superconductivity with the distorted structure and thus, potentially with an antiferromagnetically ordered state. To answer the crucial question about the coexistence of superconductivity, magnetic order and structural phase transition, further investigations into the magnetism of the doped compounds $(Ba_{1-x}K_x)Fe_2As_2$ are required.

Experimental Section

Polycrystalline samples of $(Ba_{1-x}K_x)Fe_2As_2$ with $x = 0$–1 were synthesized by heating stoichiometric mixtures of the elements (purity > 99.9 %) at 823–1223 K in alumina crucibles enclosed in silica ampoules under an argon atmosphere. To minimize the loss of potassium by evaporation, the gas volume in the crucibles was reduced by alumina inlays. The products were black metallic powders and stable in air for weeks. Sampling energy dispersive X-ray spectroscopy (EDX) measurements showed homogenous distributions of barium and potassium (± 5 %) and confirmed the compositions obtained from the Rietveld fits. X-ray powder diffraction patterns were recorded between 10 K and 300 K using a Huber G670 imaging plate detector ($Cu_{K\alpha 1}$ radiation, Ge(111) monochromator, closed-cycle helium crystat). Patterns at room temperature were indexed with tetragonal body-centered unit cells according to the $ThCr_2Si_2$-type (space group *I*4/*mmm*) or with orthorhombic face-centered unit cells (space group *Fmmm*, $a_{ortho} \approx \sqrt{2}a_{tetra} - \delta$, $b_{ortho} \approx \sqrt{2}b_{tetra} + \delta$, $c_{ortho} \approx c_{tetra}$) at low temperatures. Small amounts of FeAs were detected as an impurity phase in some samples. Crystal structures were refined by the Rietveld method using the GSAS[35] software package using Thompson–Cox–Hastings functions with asymmetry corrections as reflection profiles.[36] Electrical resistances were measured by the four-probe method on cold pressed and sintered (at 1123 K) pellets using a helium closed-cycle refrigerator. Gold wires were fixed to the sample by silver conduction paint.

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