Uniform chemical pressure effect in solid solutions
Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ and Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$

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Abstract.
The effect of alkaline earth substitution on structural parameters was studied in high-quality single crystals of Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ and Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ grown by the self-flux method. The results of single-crystal and powder x-ray diffraction measurements suggest a continuous monotonic decrease of both $a$- and $c$-axis lattice parameters, the $c/a$ tetragonal ratio, and the unit cell volume with decreasing alkaline earth atomic radius as expected by Vegard’s law. As a result, the system experiences a continuously increasing chemical pressure effect in traversing the phase diagram from $x = 0$ in Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ to $x = 1$ in Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$.

The recent discovery of high-temperature superconductivity in iron-based compounds has attracted much interest. The parent phases of these compounds generally show antiferromagnetic order that onsets between 130 K and 200 K, with superconductivity emerging when the antiferromagnetic order of the parent compounds is suppressed [1, 2, 3, 4, 5]. This proximity of magnetic and superconducting order parameters is widely thought to be a key argument for an unconventional pairing mechanism, likely mediated by spin fluctuations [6, 7] similar to the cuprates [8, 9]. But in strong contrast to the copper oxides, superconductivity in iron arsenides can be induced without changing the carrier concentration, either by applying external pressure [10, 11] or by isovalent chemical substitution. The highest $T_c$ achieved so far in these materials is $\sim 55$ K in SmO$_{1-x}$F$_x$FeAs [5] and (Sr, Ca)FeAsF [12, 13]. Oxygen-free FeAs-based compounds with the ThCr$_2$Si$_2$-type (122) structure also exhibit superconductivity induced by chemical substitution of alkali or transition metal ions [3, 14, 15, 16], the application of large pressures [11, 17, 18, 19], or lattice strain [20], with transition temperatures as high as $\sim 37$ K.

For the 122 phase, superconductivity has been induced by substituting Fe with not only 3$d$-transition metals such as Co and Ni, but also some of the 4$d$- and 5$d$-transition metals. Recently, Ru, Ir, and Pt substitution for Fe were also shown to induce superconductivity in SrFe$_2$As$_2$ and BaFe$_2$As$_2$ [21, 22, 23]. Superconductivity with $T_c \sim 31$ K has also been shown to occur by isovalent substitution of P for As [24]. This gives the opportunity to tune magnetic character without nominally changing charge carrier concentrations, for instance making the interpretation of transport coefficients much simpler than in the case of charge doping.
Figure 1. (a) Measured Ca concentration of Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ single-crystal samples as a function of nominal concentration $x$, as determined by wavelength dispersive x-ray spectroscopy (data points represent an average value of 8 scanned points for each concentration). Some of the specimens are also confirmed by energy dispersive X-ray spectroscopy (EDS). The dotted line is a guide to eye which traces $x$(measured)=$x$(nominal). (b) Typical x-ray powder diffraction pattern, shown for sample Sr$_{0.33}$Ca$_{0.67}$Fe$_2$As$_2$, obtained by using Mo-K$_\alpha$ radiation. The main peaks can be indexed with a tetragonal structure and there are no impurity phases detected within experimental accuracy. (c) Upper panel: Variation of the $a$- and $c$-axis lattice constants as a function of alkaline earth substitution in the series Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ (left half) and Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ (right half) as determined from single crystal x-ray diffraction measurements at 250 K of single-crystal samples. Corresponding $c/a$ ratio and the unit cell volume are plotted in the lower panel. In both panels, solid symbols indicate data acquired using single-crystal specimens and open symbols represent data determined by powder x-ray diffraction.

In order to investigate the possibility of applying uniform chemical pressure in a continuous manner, we have synthesized the series of solid solutions Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ and Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ by substituting isovalent alkaline earth atoms, and investigated the evolution of the crystal structure by high-resolution powder and single-crystal x-ray diffraction. Here we present our preliminary results that suggest the unit cell of the Ba-Sr-Ca substitution series experiences a monotonic uniform chemical pressure as a function of alkaline earth atomic radius.

Single-crystal samples of Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ and Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ were grown using the FeAs
self-flux method [20]. Fe was first separately pre-reacted with As via solid-state reaction of Fe (99.999%) powder with As (99.99%) powders in a quartz tube of partial atmospheric pressure of Ar. The precursor materials were mixed with elemental Sr (99.95%) with either Ba (99.95%) or Ca (99.95%) in the ratio 4:1−x : x, placed in an alumina crucible and sealed in a quartz tube under partial Ar pressure. The mixture was heated to 1150°C, slow-cooled to a lower temperature and then quenched to room temperature. Typical dimensions of as-grown single crystal specimen are ∼100 μm thickness and up to 5 mm width. Chemical analysis was performed using both energy- and wavelength-dispersive x-ray spectroscopy (WDS).

Both EDS and WDS analysis of all Ba1−xSrxCaxFe2As2 and Sr1−xCaxFe2As2 samples showed the proper 1:2:2 stoichiometry in all specimens reported herein, with no indication of impurity phases. Figure 1(a) compares the nominal alkaline earth concentration x in Sr1−xCaxFe2As2 crystals with that measured by WDS and EDS analysis, using an average value determined from 8 different spots on each specimen. As shown by the dotted line guide, the actual concentrations found by WDS are equal to the nominal values of x to within experimental error, indicating homogeneous substitution in this series of solid solutions.

Diffraction patterns were obtained by both powder and single-crystal x-ray diffraction and Rietfeld refinement (SHELXS-97) to I4/mmm structure. Powder x-ray diffraction was performed at 250 K using a Smart Apex2 diffractometer with Mo-Kα radiation and a graphite monochromator. Figure 1(b) shows a typical x-ray diffraction pattern obtained from a single-crystal sample of Sr0.3Ca0.7Fe2As2. All of the main peaks can be indexed to the ThCr2Si2 structure, with no impurity phases detected.

Table 1. Crystallographic data for SrFe2As2 and Sr0.3Ca0.7Fe2As2 determined by single-crystal x-ray diffraction at 250 K. The tetragonal structure was solved and refined using the SHELXS-97 software, yielding lattice constants with residual factor R= 1.36% and 1.95% for SrFe2As2 and Sr0.33Ca0.67Fe2As2, respectively.

| Temperature | SrFe2As2 | Sr0.33Ca0.67Fe2As2 |
|-------------|----------|-------------------|
| 250 K       | 250 K    |                   |
| Space group | I4/mmm   | I4/mmm            |
| a(Å)=b(Å)  | 3.9289(3)| 3.9066(8)         |
| c(Å)        | 12.3172(12)| 11.988(5)       |
| V(Å3)       | 190.17(4)| 182.95(9)        |
| Z           | 2        | 2                 |
| Density(g/cm3) | 6.098  | 6.045             |

Atomic parameters:

| Sr/Ca | 2a(0,0,0) | 2a(0,0,0) |
| Fe    | 4d(1/2,0,1/4) | 4d(1/2,0,1/4) |
| As    | 4e(0,0,z) | 4e(0,0,z) |
| z     | 0=0.36035(5) | z=0.36423(7) |

Atomic displacement parameters Ueq (Å²):

| Sr1/Cal | 0.0108(2) | 0.0116(5) |
| Fe1    | 0.0096(2) | 0.0125(3) |
| As1    | 0.00964(17) | 0.0119(2) |

Bond lengths and angles:

| Sr/Ca-As (Å) | 3.2677(4) × 8 | 3.2062(7) × 8 |
| Fe-As (Å)    | 2.3890(4) × 4 | 2.3855(7) × 4 |
| Fe-Fe (Å)    | 2.7782(2) × 4 | 2.7624(6) × 4 |
| As-Fe-As(deg) | 110.63(3) × 4 | 109.94(4) × 4 |
| Fe-As-Fe(deg) | 70.696(14) × 4 | 70.24(2) × 4 |

Table 1 shows the crystallographic parameters determined by single-crystal x-ray-diffraction.
at 250 K in Sr$_{0.3}$Ca$_{0.7}$Fe$_2$As$_2$. A Bruker Smart Apex2 diffractometer with Mo-K$_\alpha$ radiation, a graphite monochromator with monocarp collimator, and a CCD area detector were used for this experiment. The structure was refined with SHELXL-97 software using 1033 measured reflections of which 115 were unique and 108 observed. The final residuals were $R_1 = 1.36\%$ and 1.96% for the observed data and $wR_2 = 3.31\%$ and 4.52% for all data for SrFe$_2$As$_2$ and Sr$_{0.3}$Ca$_{0.7}$Fe$_2$As$_2$ respectively. Sr and Ca atoms were found to reside in the same site with a refined Ca:Sr = 0.33(1):0.67(1), giving the exact formula Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ from x-ray analysis.

Figure 1(c) presents the variation of the $c/a$ ratio (lower panel) with Ba-Sr and Sr-Ca concentrations determined from refinements of the single crystal x-ray diffraction data for Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ and Sr$_{1-x}$Ca$_x$Fe$_2$As$_2$ crystals taken at 250 K. Within experimental accuracy, the $a$- and $c$-axis lattice constants, the $c/a$ ratio, and the unit cell volume all show a monotonic linear decrease with alkaline earth substitution in the continuous series from BaFe$_2$As$_2$ to SrFe$_2$As$_2$ to CaFe$_2$As$_2$. This fact indicates that the whole (Ba,Sr,Ca)Fe$_2$As$_2$ series progression experiences a uniform chemical pressure effect due to the reduction of the cation size that follows Vegard’s law, as expected for the decreasing ionic radii of Ba, Sr and Ca, respectively.

The lattice parameters of Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ obtained in our experiments are consistent with the data reported in a recent study [25, 26], which found a systematic increase of $T_0$ with increasing Sr content and no superconductivity. On the other hand, substitution of arsenic for the smaller phosphorus atoms, also instituting a chemical pressure effect, induces superconductivity in BaFe$_2$As$_2$-$x$P$_x$ [25]. Thus, a pressure-volume effect is clearly an oversimplified explanation for superconductivity in BaFe$_2$As$_2$-$x$P$_x$. In the future, it will be interesting to investigate the evolution of superconductivity combining both the chemical pressure effect of alkaline earth substitution studied here and another tuning parameter that induces superconductivity in order to investigate the role of lattice density in these phenomena.

References
[1] Kamihara Y, Watanabe T, Hirano M., and Hosono H., J. Am. Chem. Soc. 130, 3296 (2008).
[2] Cruz de la C et al., 2008 Nature 453, 899.
[3] Rotter M, Tegel M, and Johrendt D, 2008 Phys. Rev. Lett. 101 107006.
[4] Saha S R, Butch N P, Kirshenbaum K, and Paglione Johnpierre, 2009 Phys. Rev. B 79 224519.
[5] Ren Z - A et al., 2008 Chin. Phys. Lett. 25 2215.
[6] Mazin I I, Schmalian J, 2009 Physica C 469 614.
[7] Christianson A D et al., 2008 Nature 456, 930.
[8] Shirane G et al., 1987 Phys. Rev. Lett. 59 1613.
[9] Keimer B et al., 1992 Phys. Rev. B 46, 14034.
[10] Okada H et al., 2008 J. Phys. Soc. Jpn. 77 113712.
[11] Alireza P L et al., 2009 J. Phys.: Condens. Matt. 21, 012208.
[12] Zhu X et al., 2009 Europhys. Lett. 85 17011.
[13] Cheng P et al., 2009 Euro Phys. Lett. 85 67003.
[14] Sasmal K et al., 2008 Phys. Rev. Lett. 101 107007.
[15] Sefat A S, Jin R, McGuire M A, Sales B C, Singhi D J, and Mandrus D, 2008 Phys. Rev. Lett. 101 117004.
[16] Leithe-Jasper A, Schnelle W, Geibel C, and Rosner H, 2008 Phys. Rev. Lett. 101 207004.
[17] Torikachvili M S, Bud’ko S L, Ni N, and Canfield P C, 2008 Phys. Rev. Lett. 101 057006.
[18] Park T et al., 2008 J. Phys.: Condens. Matt. 20 322204.
[19] Kumar M et al., 2008 Phys. Rev. B 78 184516.
[20] Saha S R, Butch N P, Kirshenbaum K, and Paglione J., 2009 Phys. Rev. Lett., 103 037005.
[21] Schnelle W et al., 2009 Phys. Rev. B 79 214516.
[22] Han F et al., 2009 Phys. Rev. B. 80 024506.
[23] Saha S R et al., 2010 J. Phys. Condens. Matt. 22 072204.
[24] Kasahara S et al., 2010 Phys. Rev. B 81 184519.
[25] Wang Z, Yang H, Ma C, Tian H, Shi H, Lu J, Zeng L, Li J, 2009 J. Phys. Condens. Matt., 21 495701.
[26] Rotter M, Hieke C, Johrendt D, 2010 Phys. Rev. B 82 014513.