ESRF	**Experiment title:** Structural phase transitions in tetragonal and collapsed tetragonal phases of MFe_2As_2 (M=Ba, Ca, Sr, Eu)	**Experiment number**: HS-3219
Beamline: ID27	**Date of experiment**: from: 2 December 2009 to 5 December 2009	**Date of report**: 24 February 2010
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Report:

The newly discovered FeAs based superconductors $LnFeAs(O_{1-x}F_x)$ (Ln=Lanthanides) and oxygen-free doped MFe_2As_2 (M=Ba, Ca, Sr, Eu) have stimulated a great deal of activity [1-10] in condensed matter research. This novel class of materials, besides existing cuprate-based high-T_c superconductors, provides yet another system for exploring the interplay between superconductivity and antiferromagnetism. The parent compounds of MFe_2As_2 system containing FeAs layers exhibit structural and magnetic phase transitions associated with Fe moments. All these compounds show strong spin density wave [7] in the temperature range of 110 to 180 K. The chemical substitutions of Ba for K, Fe for Co and application of pressure suppress the antiferromagnetic transition, resulting in the appearance of superconductivity. The emergence of superconductivity coincides with the disappearance of the antiferromagnetic transition. The spin fluctuation of Fe moments is suggested to play an important role in establishing the superconducting ground state. An important clue to the mechanism of superconductivity should be provided by high-pressure experiment on a stoichiometric sample since the application of pressure introduces no disorder.

We have carried out high pressure powder x-ray diffractions studies on MFe_2As_2 (M=Ba, Ca) using ID27 beam line up to 35 GPa. The membrane cell was used for measurements at high pressure. Helium was used as a pressure-transmitting medium in the measurements. For both the samples the data was collected up to about 37 GPa at temperatures 300 K and about 40 K. At low temperatures of about 40 K we could collect very good data MFe_2As_2 (M=Ba, Ca) at the pressure intervals of 1-2 GPa. However at 300 K we could measure only very few data points for both the samples. As reported earlier [9] we find that $CaFe_2As_2$ transform to collapsed phase at about 0.3 GPa at 40 K. However, $CaFe_2As_2$ does not show any post-collapsed phase transition on increase of pressure to 34 GPa at 40 K. For $BaFe_2As_2$, the tetragonal phase transformed to orthorhombic phase on cooling and found to remain stable up to 40 K at 1 GPa. The orthorhombic phase was found to be stable up on further increase of pressure up to 37 GPa at 40 K. At 37 GPa we have increased the temperature. We found that the orthorhombic phase of $BaFe_2As_2$ transformed to collapsed phase at 37 GPa and 200 K. The temperature was further increased to 300 K. While releasing the pressure we could get only two data points at 37 GPa and 30 GPa at 300 K in the collapsed phase of $BaFe_2As_2$. We noticed that below

20 GPa at 300 K the collapsed phase reverted back to the normal tetragonal phase. We could not properly characterise the collapsed phase of $BaFe_2As_2$ and $CaFe_2As_2$ at 300 K.

Lattice parameter obtained after Rietveld anaysis for $BaFe_2As_2$ and CaFe2As2 are shown in Fig. 1 and 2 respectively. In addition to this Rietveld refinment of some of the selected diffraction data for $BaFe_2As_2$ and $CaFe_2As_2$. are shown in Fig. 3.

Our experiments show that in case of $BaFe_2As_2$ the transformation to collapsed tetragonal phase occurs at relatively lower pressure when it is measured at high temperature (30 GPa, 300 K) than at low temperature (at 40 K, no transformation was seen up to 37 GPa). On the other hand, $CaFe_2As_2$ undergoes [9] the transition to the collapsed tetragonal phase at 0.3 GPa at 50 K. However at room temperature, a fairly high pressure (about 1.8 GPa) is necessary to induce the phase transition into the collapsed phase. The phase transformation behaviour in MFe_2As_2 (M=Ba, Ca, Sr, Eu) seems to depend on the ionic size of M atom. So it is necessary to investigate the high pressure behaviour of $SrFe_2As_2$ and $EuFe_2As_2$.

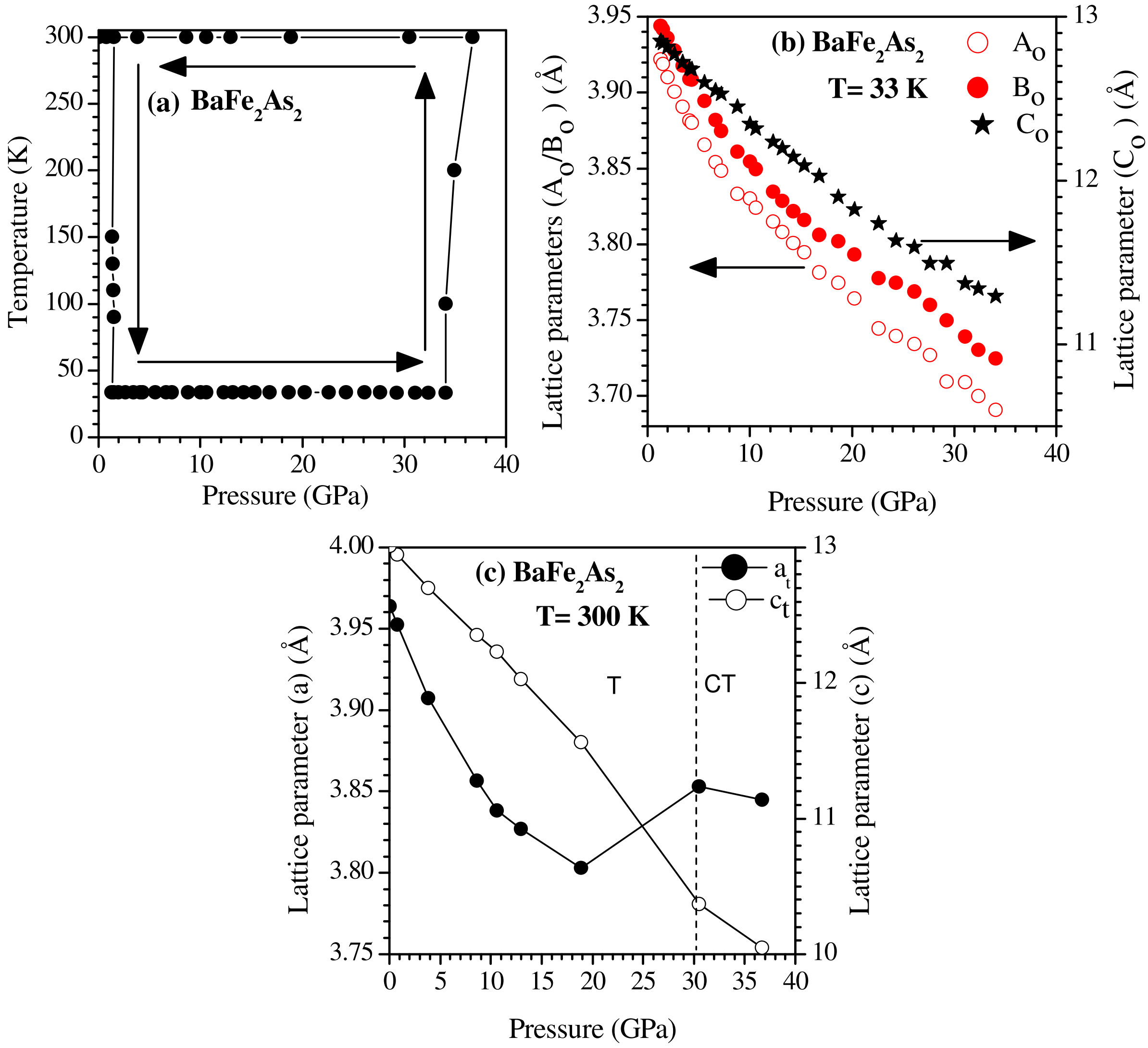

Fig. 1(a) The pressure-temperature conditions for measurement of $BaFe_2As_2$. Arrow indicates the sequence of measurements during the experiment. The measurements are performed under hydrostatic condition. The variation of lattice parameters with pressure at **(b)** 33 K and **(c)** 300 K. For easy comparison, orthorhombic lattice parameters (a, b, and c) are converted into the equivalent tetragonal lattice parameters (A_o, B_o and C_o) using the relation $A_o = a/\sqrt{2}$, $B_o=b/\sqrt{2}$ and $C_o=c$.

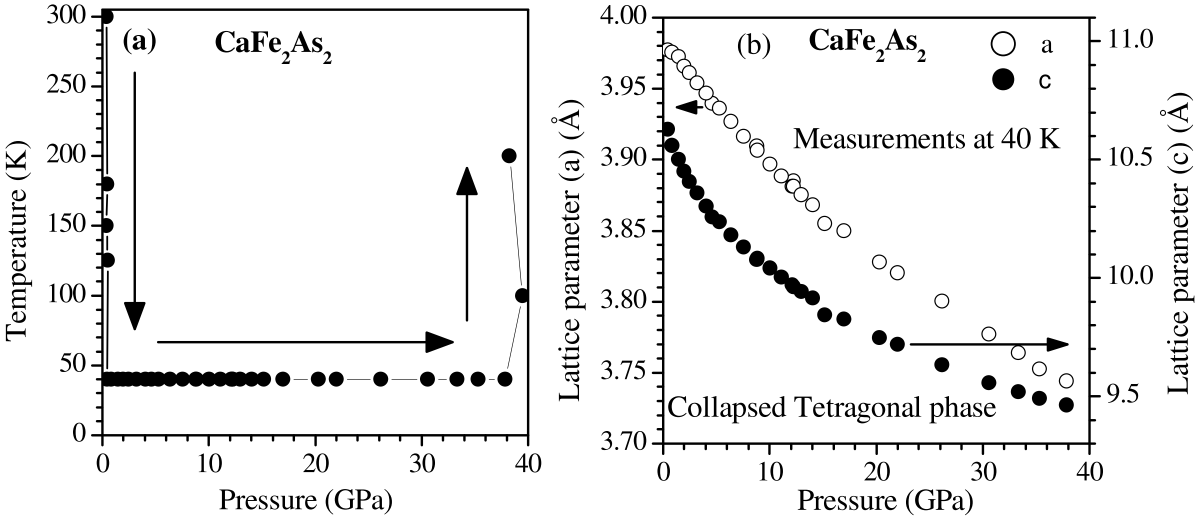

Fig. 2 **(a)** The pressure-temperature measurements condition for $CaFe_2As_2$. Arrow indicates the sequence of measurements during the experiment. The measurements are performed under hydrostatic condition. **(b)** Variation of lattice parameters with pressure at 40 K.

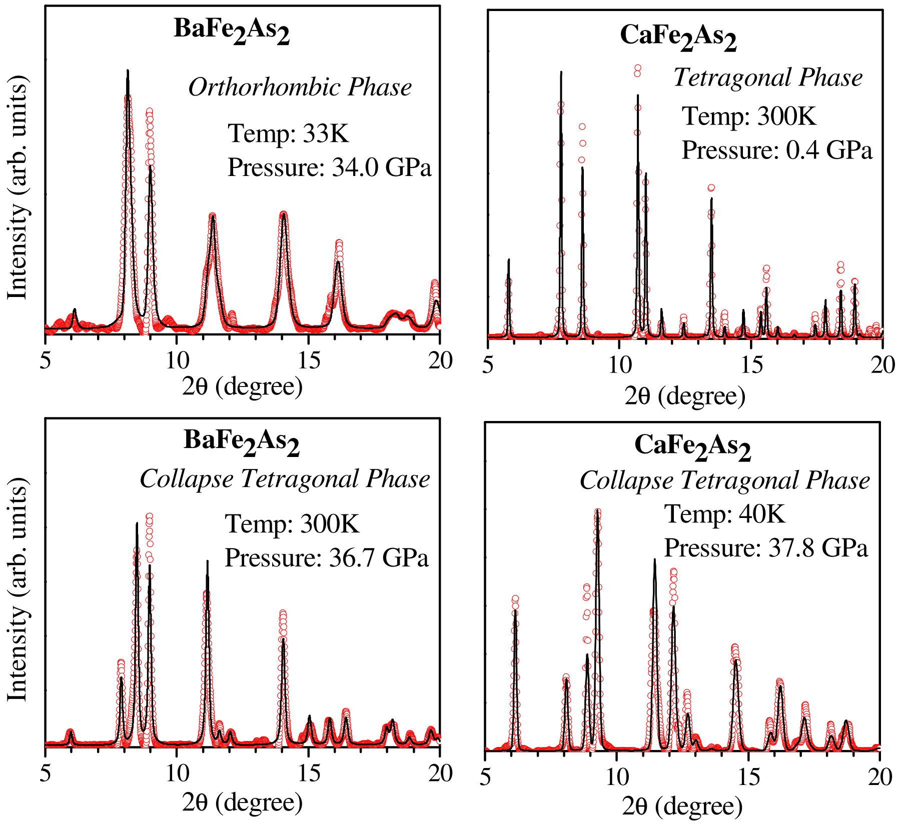

Fig. 3 Rietveld refinment of some of the selected diffraction data of $BaFe_2As_2$ and $CaFe_2As_2$. The open circles and solid lines correspond to experimental data and fitted profiles.

[1] Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, Nature **453**, 376 (2008).
[3] M. Rotter et al., Phys. Rev. Lett. **101**, 107006 (2008).
[4] M. S. Torikachvili, N. Ni, S. L. Bud'ko and P. C. Canfield, Phys. Rev. Lett. **101**, 057006 (2008).
[5] P. L. Alireza et al, J. Phys.: Condens. Matter **21**, 012208 (2008).
[7] Y. Su et al, Phys. Rev. B **79**, 064504 (2009).
[8] A. Kreyssig et al, Phys. Rev. B **78**, 184517 (2008).
[9] A. I. Goldman et al, Phys. Rev. B **79**, 024513 (2009).
[10] F Ronning et al, J. Phys.: Condens. Matter **20**, 322201 (2008).