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Pressure-driven Phase Transition in CaFeAsF at 40 and 300 K


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We carried out systematic investigation of high pressure crystal structure and structural phase transition up to 46 GPa at 40 K and 25 GPa at 300 K in CaFeAsF using powder synchrotron x-ray diffraction experiments. Rietveld analysis of the diffraction data at 40 K reveals a structural phase transition from an orthorhombic to a monoclinic phase at \( P_c = 13.7 \) GPa, while increasing pressure. The transition to a lower symmetry phase (orthorhombic to monoclinic) in this 1111 compound under pressure is in contrast with the transition to a high symmetry phase (orthorhombic to tetragonal) as observed in the ‘122’ type compounds. On heating from 40 K at high pressure, CaFeAsF undergoes a monoclinic to tetragonal phase transition around 25 GPa and 200 K. Further, it does not show any post-tetragonal phase transition, as observed in ‘122’ compounds (CaFe2As2, BaFe2As2), and remains in the tetragonal phase up to 25 GPa at 300 K. The dP/dT slope is found to be positive for CaFeAsF and CaFe2As2, unlike a negative gradient was found in case of BaFe2As2.

1. Introduction

Iron based superconductor compounds have generated enormous interest because these materials are the first non-copper oxide superconductors with superconducting transition temperature (\( T_c \)) exceeding 50 K [1-9]. These compounds occur in five different structural classes. Among them the superconductors with the FeAs-1111 structure are known to have the highest superconducting transition temperature. The highest \( T_c \) reported so far is about 56 K in Sm-doped SrFeAsF compounds [3]. In SrFeAsF, superconductivity could also emerge by either doping with cobalt directly into the FeAs-layer, or by partial replacement of Sr with rare earth elements (Lanthanum). While, for CaFeAsF, superconductivity was also realized by doping with 3d transition metals (Co and Ni) into the iron sites in the FeAs-layer with the highest \( T_c \) of about 22 K in the case of Co-doping [4]. The mechanism of superconductivity in the FeAs-based system remains unclear yet.

At ambient condition, these compounds crystallize in tetragonal symmetry with no magnetic order (i.e paramagnetic in nature). The parent compounds of iron-pnictides undergo a first or second
order structural transition below room temperature (typically in the range of 100-210 K), from
tetragonal to orthorhombic structure, and magnetic transition from non-magnetic to stripe antiferro
magnetic structure. The antiferromagnetic ordering can be suppressed by various ways, namely, by
changing the carrier concentration, by charge neutral doping [3-5], and by applying external pressure
[6-7]. High pressure experiments play an important role in the field of superconductivity by three
primary ways: (i) to test theories of superconductivity and reveal important systematic, (ii) to improve
the properties of known superconductors and (iii) to create new superconductors. In this paper, we
report systematic investigation of high pressure crystal structures and a structural phase transition in
CaFeAsF at ambient and low temperature using powder synchrotron x-ray diffraction experiments and
Rietveld analysis of the diffraction data. A detailed manuscript including this work will be published
elsewhere [10].

2. Experiment
The x-ray diffraction studies were performed on the CaFeAsF powder samples at the ID27
high-pressure beam line of the European Synchrotron Radiation Facility using a monochromatic beam
(λ = 0.3738 Å ) focused to 3×2 μm². The diamond anvil cells with 150 μm cullet diamonds with
stainless steel gasket and helium as pressure transmitting media were used, which provides the best
hydrostatic conditions. During the measurements, we determined the pressure using two ruby balls.
The pressure difference determined from ruby balls was always below 0.1–0.2 GPa. The diffraction
patterns were collected with a CCD camera and the intensity vs 2θ patterns were obtained using the
FIT2D software. The structural refinements were performed using the Rietveld refinement program
FULLPROF [11]. During the measurement, the CaFeAsF sample was first cooled to 40 K, and then
pressure was increased. The diffraction patterns indicate preferred orientation of the samples along
[211] direction.

3. Results and Discussion
3.1 Structural response of CaFeAsF to Pressure at Low Temperature (40 K)
Inspection of powder synchrotron x-ray diffraction profile of the CaFeAsF at ambient
condition confirmed the primitive tetragonal symmetry with space group P4/nmm which is consistent
with the literature. On cooling, splitting of a (220) peak of the tetragonal phase at 300 K
unambiguously confirms the orthorhombic structure at 40 K, as shown in the inset of Figure 1. The
pressure-dependent powder x-ray diffraction measurements were carried out at 40 K. Detailed analysis
of diffraction patterns reveal that these have dissimilar broadening in various peaks with pressure. The
most pronounce changes occur in peak around 2θ=11 degree. Observations of dissimilar broadening in
diffraction profiles suggest a possibility of a structural phase transition with pressure. To explore the
possibility, we refined powder diffraction data using orthorhombic structure with space group Cmna.
We found that all the diffraction patterns could be successfully accounted only for up to 12 GPa. A
progressive worsening of the quality of the Rietveld fits with increasing pressure was found for
pressure above 12 GPa. The most apparent signature of the subtle structural transformation that occurs
at above 12 GPa is an inability of the orthorhombic structure (space group Cmna) to account
satisfactory for the peaks around 11 degree, shown in Fig. 2 (a). Extra broadening (splitting) of the
peaks suggests either lowering of the symmetry or coexistence of another high symmetry phase.
Recently, we found that in BaFe2As2 orthorhombic and tetragonal phases coexist over a large
pressure range above 29 GPa at 33 K [5]. In view of this, we made an attempt to refine diffraction data
using phase coexistence model. We found that if the profile around 11.5 degree was fitted (forcefully),
the calculated peaks around 2.5, 7.9, 9.8 degree arising due to the tetragonal phase are not observed in
the experiment data (see Fig. 2(b)). This unsatisfactory quality of the Rietveld fit clearly ruled out the
possibility to the phase coexistence.
Critical inspection of diffraction data only show the splitting in some peaks but not any additional superlattice peak in diffraction patterns. Absence of superlattice peak clearly ruled out the possibilities of integral multiplication of lattice parameters with respect to orthorhombic cell. Thus, it suggests the lowering of symmetry from the orthorhombic structure with space group \( \text{Cmma} \). We have further explored various possibilities, namely, orthorhombic symmetry with space group \( \text{Pbcm}, \text{Pmmn} \); monoclinic structure with space group \( \text{P12/1} \) etc. (see Fig. 2 (c) and (d)) to identify the correct space group. We found that orthorhombic space groups could not fit the structural data very well, but the monoclinic structure with space group \( \text{P12/1} \) (in \( \text{cab} \) setting \( \text{P112/1} \)) could successfully index all the peaks (see Fig. 2(c)). It is well documented in the literature that many iso-structural \( \text{Fe} \)-based materials undergo a structural phase transition to the monoclinic phase with temperature and pressure [8]. Rietveld refinements employing this structural model are satisfactory for all the diffraction patterns up to the highest pressure measured by us. A careful inspection and analysis of diffraction data reveal that \( \text{CaFeAsF} \) transforms to the monoclinic structure at \( P_c = 13.7 \) GPa even

**Fig 1.** (Color online) Observed (black solid circle), calculated (continuous red line), and difference (bottom blue line) profiles obtained after the Rietveld refinement of \( \text{CaFeAsF} \) at 5.8 GPa & 40 K, in orthorhombic phase (space group \( \text{Cmma} \)). Insets show the (220) reflection of the tetragonal phase and its splitting/broadening at 40K. This is an unambiguous signature for the orthorhombic structure at low temperature.

**Fig 2.** (Color online) Observed (solid black circle) and calculated (continuous red line profiles obtained after the Rietveld refinement of \( \text{CaFeAsF} \) at 40 K & 20.3 GPa using different models namely: (a) an orthorhombic (\( \text{Cmma} \)), (b) a combination of tetragonal (\( \text{P4/nmm} \)) and an orthorhombic (\( \text{Cmma} \)); (c) monoclinic (\( \text{P2/n} \)) and (d) an orthorhombic (\( \text{Pmmn} \)) phases, respectively.

**Fig 3.** (Color online) Pressure evolution of the normalized lattice parameters of \( \text{CaFeAsF} \) at 40 K obtained from Rietveld analysis.
though the monoclinic distortion is quite small. The monoclinic angle (β) as a function of pressure shows a sharp discontinuity at the transition pressure at 13.7 GPa and very small further change from 90.5° to 91.2° on increase in pressure up to 46.2 GPa. Discontinuity in the pressure evolution of the monoclinic angle clearly suggests a first order phase transition in CaFeAsF. Figure 3 depicts the pressure evolutions of the normalized structural parameters of CaFeAsF at 40 K. It is evident from this figure that the response of the lattice parameters to pressure is strongly anisotropic with the interlayer spacing (along <001>) showing a significantly larger contraction than the basal plane dimensions (along <100> and <010>).

3.2 Structural response of CaFeAsF to Pressure at High Temperature (300 K)

Due to experimental limitations, we could not increase pressure on CaFeAsF beyond 46 GPa at 40 K. However, to see the effect of temperature on the newly stabilized monoclinic phase in CaFeAsF (at 40 K and around 40 GPa), we carried out measurements at different conditions and details are given elsewhere [10]. Careful analysis of the diffraction data show that there is an abrupt change in the diffraction pattern at 25 GPa and 200 K, at which the monoclinic splitting/broadening in Bragg reflections around 11.5° and 16.5° disappears. Detailed Rietveld analyses of the diffraction data reveals that the sample undergoes a structural phase transition from the monoclinic to the tetragonal phase at around 25 GPa and 200 K. It retains in the tetragonal phase at 25 GPa and 300 K. However, this behaviour of dPc/dT ma y not hold for Ba/Sr compounds. In addition to this, the transition to a lower symmetry phase (orthorhombic to monoclinic) in the ‘1111’ compounds (CaFeAsF/SrFeAsF) under pressure is in contrast with the transition to a high symmetry phase (orthorhombic to tetragonal) in the ‘122’ (Ba2Fe2As2/ CaFe2As2)-type compounds.

4. Conclusions

In summary, we have carried out systematic investigation of high-pressure crystal structures and structural phase transition upto 46 GPa at 40 K and 25 GPa at 300 K in CaFeAsF using powder synchrotron x-ray diffraction experiments and Rietveld analysis of the diffraction data. It is interesting to note that at 40 K, CaFeAsF shows the orthorhombic to monoclinic phase transition at Pc =13.7 GPa, whereas at room temperature the tetragonal phase is stable upto 25 GPa. The observation of dPc/dT>0 is similar to that observed in CaFe2As2 in which a collapsed tetragonal phase transition occurs at a lower pressure (0.3 GPa) at a lower temperature (50 K), in comparison with 1.7 GPa at 300 K. However, this behaviour of dPc/dT may not hold for Ba/Sr compounds. In addition to this, the transition to a lower symmetry phase (orthorhombic to monoclinic) in the ‘1111’ compounds (CaFeAsF/SrFeAsF) under pressure is in contrast with the transition to a high symmetry phase (orthorhombic to tetragonal) in the ‘122’ (Ba2Fe2As2/ CaFe2As2)-type compounds.

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