



Thermal expansion behaviour and phase stability of AFe_2As_2 ($A=Ca, Sr$ and Eu) using powder diffraction technique

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Abstract. The thermal expansibilities and phase stabilities of AFe_2As_2 ($A = Ca, Sr$ and Eu) have been investigated by powder diffraction techniques in the temperature range 5–600 K. We found the anisotropic thermal expansivities with temperature for all the compounds. The lattice parameter in the tetragonal phase (A_T) of $CaFe_2As_2$ contracts with increasing temperature, whereas C_T expands. The rate of contraction in A_T is lower than the rate of expansion in C_T . Other compounds show normal thermal expansion behaviour along both a - and c -axes. In-plane expansion (i.e., along the a -axis) is found to be the smallest for $EuFe_2As_2$ and the highest for $BaFe_2As_2$. However, the rate of change of thermal expansivities along out-of-plane (i.e., along the c -axis) is higher as we go from Ba, Sr, Eu and Ca , respectively. Above 600 K, we notice the appearance/disappearance of certain reflections which suggest that tetragonal phase is not stable above this temperature for these compounds.

Keywords. Ternary, quaternary and multinary compounds (Fe-based superconductor); crystallographic aspects of phase transformations; X-ray diffraction; neutron diffraction and scattering.

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1. Introduction

The discovery of Fe-based superconductors by Hosono group [1] opened a new frontier of superconductivity [2–6]. The key player in these materials is the element iron (Fe), which was earlier known to be an element for destabilization of superconductivity.

Compositionally, various types of Fe-based superconductors have been reported in literature. But, crystallographically, their parent materials have been classified into five types [4]. A wide variety of experimental and theoretical techniques have been used to understand physics of 1111 and 122 types of Fe-based compounds [3–33]. At ambient pressure, they possess similar sequence of structural phase transitions with decreasing temperature (tetragonal to orthorhombic). But, our recent high-pressure synchrotron study on these compounds revealed a different phase transition sequence [20]. The parent materials of both 1111 and 122 families do not exhibit superconductivity at ambient pressure, but become superconductors by the application of chemical or external pressure.

Analysis of structural and physical properties of CaFe_2As_2 , BaFe_2As_2 , SrFe_2As_2 and EuFe_2As_2 compounds suggest that the tetragonal to orthorhombic phase transition in these materials occurs at about 170, 140, 205 and 210 K [13,14,30] respectively. At ambient conditions, they crystallize into tetragonal symmetry with space group $I4/mmm$. On cooling, they transform to orthorhombic structure, which is also accompanied by a magnetic transition. These compounds have been investigated extensively by different techniques. For example, using single-crystal X-ray diffraction technique, Ni *et al* [12] have shown that CaFe_2As_2 undergoes tetragonal to orthorhombic phase transition at 170 K and it is of first-order type with hysteresis and coexistence over a temperature range of 2–3 K. Physical properties viz., specific heat, electrical resistance and magnetic susceptibility exhibit an anomaly at structural and magnetic phase transition temperature (170 K) [10,12]. Ran *et al* [33] have shown that the tetragonal-to-orthorhombic phase transition can be suppressed by manipulating the annealing temperature. Recent transmission electron microscopy (TEM) studies [19] reveal that CaFe_2As_2 has more complex microstructure properties than SrFe_2As_2 .

To investigate tetragonal phase stability at high temperature, X-ray diffraction measurements [34] on 122 compounds viz., CaFe_2As_2 and BaFe_2As_2 were carried out. We found that the lattice parameters of BaFe_2As_2 monotonically increase with increasing temperature in the tetragonal phase. In contrast, for CaFe_2As_2 , though the c -parameter monotonically increases with increasing temperature, the a -parameter decreases with increasing temperature up to 600 K.

Temperature-dependent structural parameters of CaFe_2As_2 are also investigated by Ni *et al* [12] but only between 4 and 210 K. The structural parameter behaviour in the temperature range 210–300 K is still missing, which is crucial to understand the anomalous behaviour of a -lattice parameter observed above 300 K. Keeping this in mind, in the present study, we have carried out systematic temperature-dependent X-ray (10–300 K) and neutron powder diffraction (4–300 K) measurements. Temperature dependence of structure evolution and structural parameters has been examined in detail. Neutron diffraction of materials offers certain advantages over X-rays, especially, in the accurate determination of the atomic positions and thermal parameters. We have also carried out diffraction measurements up to 600 K on SrFe_2As_2 and EuFe_2As_2 , that agree with the published results below 300 K. Usual thermal expansion behaviour is observed in all the lattice parameters of CaFe_2As_2 , SrFe_2As_2 and EuFe_2As_2 compounds except the a -lattice parameter of CaFe_2As_2 . Temperature-dependent magnetization of polycrystalline CaFe_2As_2 sample shows weak anomalies below 170 K. This behaviour of the polycrystalline sample is in contrast with that of a single crystal (synthesized using Sn flux) reported earlier.

2. Experimental

The polycrystalline samples were prepared by Matsuishi and Hosono using solid-state reaction method as reported in our earlier work [21]. The X-ray and neutron powder diffraction measurements at ambient temperature confirmed the sample to be in a single phase. All the reflections can be indexed with tetragonal symmetry with space group $I4/mmm$ consistent with the published reports [10,12]. The neutron powder diffraction is performed as a function of temperature at the Dhruva reactor at Bhabha Atomic Research Centre, Trombay, India. The structural refinements were performed using the Rietveld refinement program FULLPROF [35]. Magnetization measurements were performed using a 9 Tesla PPMS-VSM (make Quantum Design) at UGC-DAE CSR, Mumbai.

3. Results and discussion

Figure 1 depicts the evolution of the (1 1 2) and (0 0 8) profiles (indexed with tetragonal phase) for powder diffraction data as a function of temperature for $CaFe_2As_2$, $SrFe_2As_2$ and $EuFe_2As_2$ respectively. It is evident from this figure that diffraction patterns show dramatic change with temperature. For example, below 175 K, for $CaFe_2As_2$, (1 1 2) profile first broadens up to 95 K and then splits into two peaks. This is an unambiguous signature for the stabilization of orthorhombic phase. It is also seen that the intensity of the (0 0 8) reflection ($Q \approx 4.35 \text{ \AA}^{-1}$) of the tetragonal phase decreases on lowering the temperature and shifts towards higher Q values. Similar observation was found for $SrFe_2As_2$ and $EuFe_2As_2$. It is important to note that for $CaFe_2As_2$, an additional peak

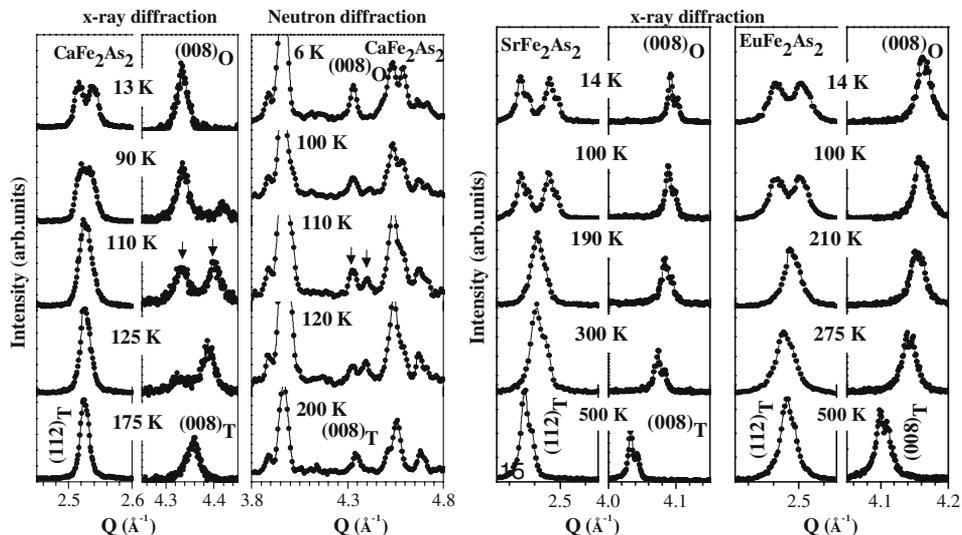


Figure 1. Evolution of the diffraction patterns for $CaFe_2As_2$ (left two panels), $SrFe_2As_2$ (middle panel) and $EuFe_2As_2$ (right panel) at selected temperature. Characteristic reflections of both phases are marked with arrows for $CaFe_2As_2$. Only relevant part of the patterns is shown for clarity.

around $Q \approx 4.32 \text{ \AA}^{-1}$ (for temperatures $\leq 125 \text{ K}$) appears and its intensity increases on lowering the temperature. It is evident from figure 1b, that powder neutron diffraction patterns also show dramatic changes with temperature especially in terms of dissimilar broadening, intensity and splitting of various peaks. Even in powder X-ray diffraction, we have noticed the appearance of an additional reflection around $Q \approx 4.32 \text{ \AA}^{-1}$ below 130 K, corresponding to the (0 0 8) reflection of tetragonal phase for CaFe_2As_2 . Further, the intensity of this peak increases gradually with decrease of temperature. It is to be noted that this peak could not be assigned to either the orthorhombic or the tetragonal phases. Detailed features of the phase transition and its behaviour are examined by analysing the powder diffraction data at various temperatures and the results are discussed below. At low temperatures, we also observed additional reflections in neutron patterns due to the magnetic ordering in the sample.

Rietveld refinement of the powder diffraction data of CaFe_2As_2 shows that the temperature-dependent X-ray and neutron diffraction patterns could be indexed using the tetragonal symmetry from 300 to 175 K. The splitting of the (1 1 2) peak of tetragonal phase in powder diffraction patterns indicates a structural phase transition from tetragonal to orthorhombic phase at 170 K which is well documented in literature. Hence, we made an attempt to refine the data using orthorhombic structure with space group Fmmm below this temperature. However, all the peaks could not be accounted for in refinement with only one phase, i.e. either the orthorhombic or the tetragonal phase. Instead, a two-phase refinement with both the orthorhombic (Fmmm) and tetragonal (I4/mmm) space groups resulted in a better fit and all the observed diffraction peaks could be clearly indexed. Rietveld refinement (figure 2) of neutron and X-ray powder diffraction data (in terms of $Q (\text{\AA}^{-1})$, which enables an easy comparison between them) shows unambiguous evidence for phase coexistence. This indicates that structural phase transition from the orthorhombic to the tetragonal phase is of first order in nature. Rietveld refinements employing this two-phase model are satisfactory for all the diffraction patterns up

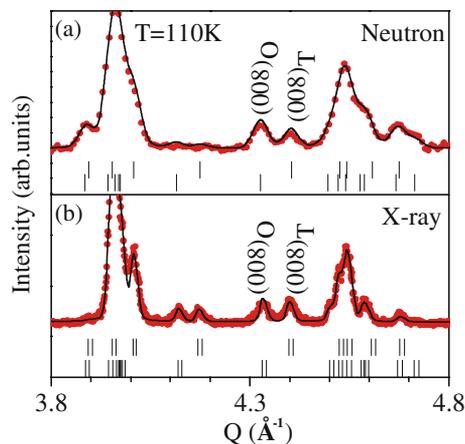


Figure 2. Observed (dot) and calculated (continuous line) profiles obtained after the Rietveld refinement of CaFe_2As_2 using both orthorhombic (space group Fmmm) and tetragonal phases (space group I4/mmm) at 110 K.

to the lowest temperature measured by us for X-ray (12 K) and neutron (6 K) data. The percentage of the orthorhombic phase fraction was found to increase on lowering the temperature. Rietveld analysis on the neutron data has also been carried out for determining the magnetic structure in the orthorhombic phase at 6 K. We found that the Fe moment is $0.83(3)\mu_B$ along the longer a -axis with the magnetic propagation vector along $(1\ 0\ 1)$. The obtained moment and propagation vector are consistent with literature values [11,30]. In all Rietveld refinements, data over full angular range have been used, although only a limited range is shown for clarity.

On the other hand, Rietveld refinement of the powder diffraction data of $SrFe_2As_2$ and $EuFe_2As_2$ do not show phase coexistence. The powder diffraction patterns could be indexed using the tetragonal ($T > 200$ K) and orthorhombic ($T < 200$ K) symmetries and documented in literature as well. On heating above 600 K, we notice the appearance/disappearance of certain reflections and suggest that tetragonal phase is not stable above this temperature. We have tried to index these peaks but our attempt was not successful. A probable cause could be the variation in the stoichiometry of materials at high temperatures due to vapourization of As.

Figure 3 shows evolution of structural parameters of tetragonal and orthorhombic phases as a function of temperature. It is evident from this figure that the a -lattice parameter (a_t) of the tetragonal phase increases with decreasing temperature in the entire temperature range. On the other hand, the c -parameter (c_t) of the tetragonal phase decreases with decreasing temperature up to 50 K, below which it becomes nearly independent of temperature. For the orthorhombic phase, the lattice parameter a_o increases and b_o decreases with decreasing temperature, whereas c_o is nearly constant up to 6(12) K in neutron (X-ray) measurements. It is clear that the rate of change of lattice parameters in the temperature range 120–170 K is higher compared to that in the remaining temperatures. It is also noticed that the unit cell volume of the tetragonal phase (figure 4a) decreases with decreasing temperature down to 90 K, below which it increases. In contrast, unit cell volume of the orthorhombic phase is nearly constant with the temperature. Also, it is important to note that the orthorhombic phase has higher unit cell volume compared to that of tetragonal phase at all the temperatures. The phase fraction obtained as a function of temperature for the tetragonal phase is shown in figure 4b. On

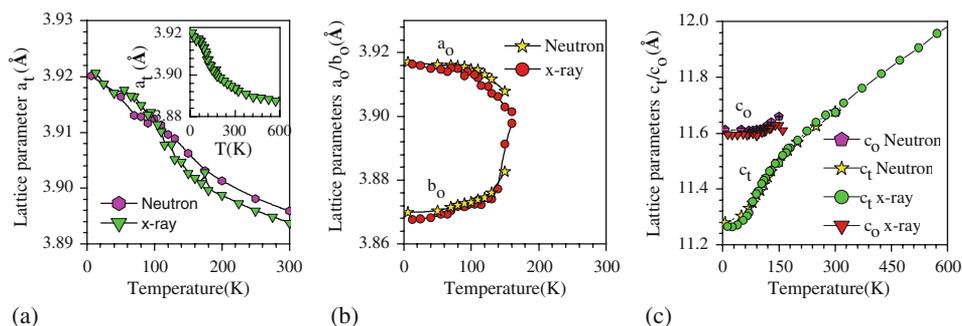


Figure 3. Evolution of the obtained lattice parameters from Rietveld refinement for different phases. The subscripts t and o refer to the tetragonal and orthorhombic phases respectively in all the figures.

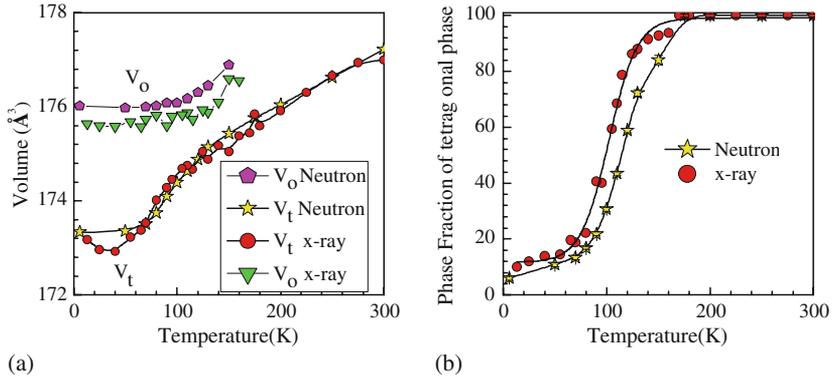


Figure 4. Evolution with temperature of the (a) unit cell volume and (b) phase fraction of the tetragonal phase. For the sake of easy comparison with the tetragonal phase, the unit cell volume of the orthorhombic phase is divided by 2.

increasing the temperature, the fraction for the tetragonal phase increases gradually up to 100 K with an abrupt increase above 100 K. Rietveld refinement of the diffraction data (figure 2) clearly reveals that for $T = 6$ K, the majority phase is orthorhombic (95%). In other words, the sample does not transform completely even at the lowest temperature for which data is recorded. It is known that the transition between the tetragonal and orthorhombic structures, as well as their coexistence over a range of temperatures, depend on the conditions of sample preparation [33]. In our case, we have observed the coexistence over a wide range of temperatures that has enabled us to determine the structural parameters as well as the thermal expansivities in both the phases. The structural data (at various temperatures) available previously in literature are in good agreement with present work.

In order to further emphasize the anomalous behaviour of CaFe_2As_2 , we have also examined the temperature variation of lattice parameters of other members of the family, namely, SrFe_2As_2 and EuFe_2As_2 . We found that a_t of the tetragonal phase of both the compounds decreases with decreasing temperature in the entire temperature range (figure 5), in contrast with CaFe_2As_2 . The c_t of the tetragonal and c_o of the orthorhombic phases for both the compounds decrease while cooling with an anomaly at respective transition temperatures. The behaviour of a_o and b_o of the orthorhombic phase is found to be consistent with that reported in literature. These results do not indicate the coexistence of phases over a wide range of temperature in SrFe_2As_2 and EuFe_2As_2 compounds unlike in the CaFe_2As_2 compound and are consistent with literature [36]. However, the measurements on SrFe_2As_2 single crystal showed phase coexistence and this discrepancy between polycrystalline and single crystal data was well explained by Loudon *et al* [37] by using electron microscopy.

Figure 6 depicts the anisotropic thermal expansivities (relative to the values at $T = 0$ K) i.e., $A_T = (a_t(T) - a_t(0))/a_t(0)$ and $C_T = (c_t(T) - c_t(0))/c_t(0)$ with temperature for all the compounds. It is clear from this figure that A_T of CaFe_2As_2 contracts with increasing temperature, whereas C_T expands. The rate of contraction in A_T is lower than the rate of expansion in C_T . Other compounds show normal thermal expansion behaviour along both a - and c -axes. It may be noted that the in-plane expansion (i.e., along the a -axis) is

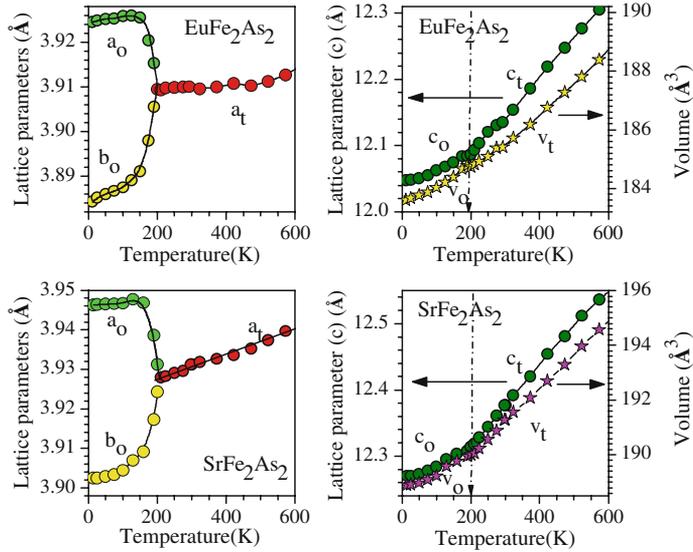


Figure 5. Evolution of the structural parameters obtained from Rietveld refinement for $SrFe_2As_2$ and $EuFe_2As_2$ for different phases.

found to be the smallest for $EuFe_2As_2$ and the highest for $BaFe_2As_2$. However, the rate of change of thermal expansivities out-of-plane (i.e., along the c -axis) is higher as we go from compounds of Ba, Sr, Eu and Ca, respectively.

For a deeper understanding of the behaviour of tetragonal-to-orthorhombic phase transition from microscopic point of view, we identify the symmetry mode (Γ_1^+), which characterizes this transformation. The program AMPLIMODES [38] was used to calculate the magnitude of the (Γ_1^+) distortion mode of Fmmm and also the degree of lattice distortion (S), which is the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). The results are shown in figure 7. The (Γ_1^+) mode corresponds to a symmetric breathing mode (see figure 8) bringing the change in z -coordinate of the As atoms only. This could be treated as an order parameter for the orthorhombic-to-tetragonal phase transition.

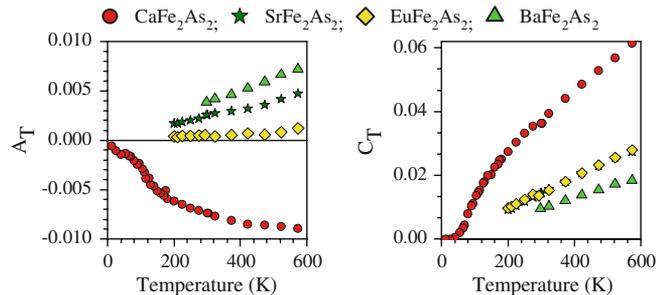


Figure 6. Evolution of the observed anisotropic thermal expansivities with temperature for the tetragonal phase.

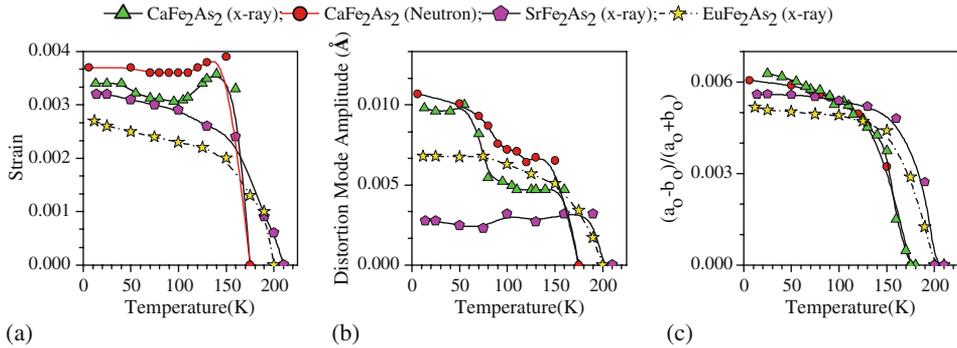


Figure 7. Variation of the (a) strain and (b) amplitude of distortion mode, as calculated using AMPLIMODES for CaFe_2As_2 , SrFe_2As_2 and EuFe_2As_2 . Temperature dependence of the orthorhombic splitting is shown in (c).

For CaFe_2As_2 , the lattice strain increases sharply with decrease in temperature up to about 140 K and becomes invariant below this temperature (figure 7a). For SrFe_2As_2 and EuFe_2As_2 , strain increases with decreasing temperature but at a different rate. The distortion of the amplitude mode also exhibits the anomalous behaviour for CaFe_2As_2 . The orthorhombic splitting $[(a_0 - b_0)/(a_0 + b_0)]$ could be treated as an additional order parameter for orthorhombic-to-tetragonal phase transition. Figure 7c depicts the temperature dependence of the orthorhombic splitting $[(a_0 - b_0)/(a_0 + b_0)]$ for CaFe_2As_2 , SrFe_2As_2 and EuFe_2As_2 , respectively. We found that the orthorhombic splitting abruptly increases with decreasing temperature up to 150 K and then the rate of increment is slower. Thus,

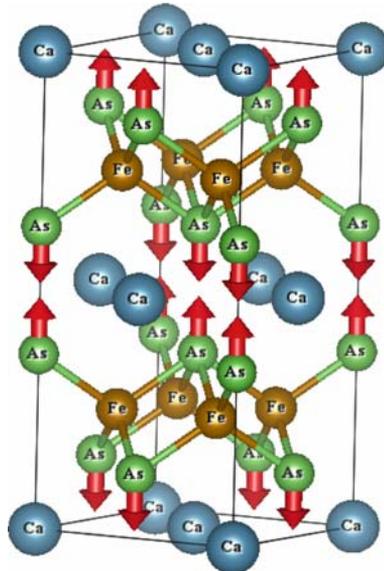


Figure 8. Illustration of Γ_1^+ mode corresponding to a symmetric breathing mode for CaFe_2As_2 .

our study shows unambiguous evidence for the presence of tetragonal phase coexistence with the orthorhombic phase over a wide range of temperatures in CaFe_2As_2 contrary to literature [33]. The discrepancy may be associated with sample preparation method and will be discussed later.

For a proper understanding of the properties of the materials, the structural information, as obtained from diffraction techniques, should be supplemented and supported by other techniques. Physical property measurement like magnetization offers a unique opportunity to reach a comprehensive conclusion regarding the stability of magnetic phase. With this aim in mind, we performed magnetization experiment which we discuss below.

Figure 9a shows the magnetization (M) curves of polycrystalline CaFe_2As_2 measured in a magnetic field of $H = 1$ kOe, using zero-field-cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) protocols. As the temperature is lowered from 300 K, the magnetization of the polycrystalline sample shows a clear transition to AFM state as indicated by the sharp rise in FCC, ZFC and FCW curves in the temperature range of 150–165 K. On further lowering of the temperature, magnetization decreases showing a minimum around 100 K. Below this temperature, magnetization shows a Curie–Weiss-like behaviour, increasing rapidly with decreasing temperature. It is well documented in literature that CaFe_2As_2 sample prepared by FeAs flux method shows Curie–Weiss-like behaviour at low temperatures [33,39]. The anomaly observed at 150 K in the present study is similar to the magnetization data of the CaFe_2As_2 single crystal grown out of Sn flux having a strong anomaly at ~ 169 K in the $H\parallel ab$ plane and $H\parallel c$ only [12]. Thermal hysteresis between the cooling (FCC – red color, ~ 151 K) and warming (FCW green colour, ~ 161 K), magnified view of which is shown in the inset of figure 9a, provides one of the clearest evidence for the first-order tetragonal-to-orthorhombic structural transition. Figure 8b shows the M vs. H isotherms at different temperatures. A very small hysteresis (± 65 Oe) was noticed in the M vs. H data only

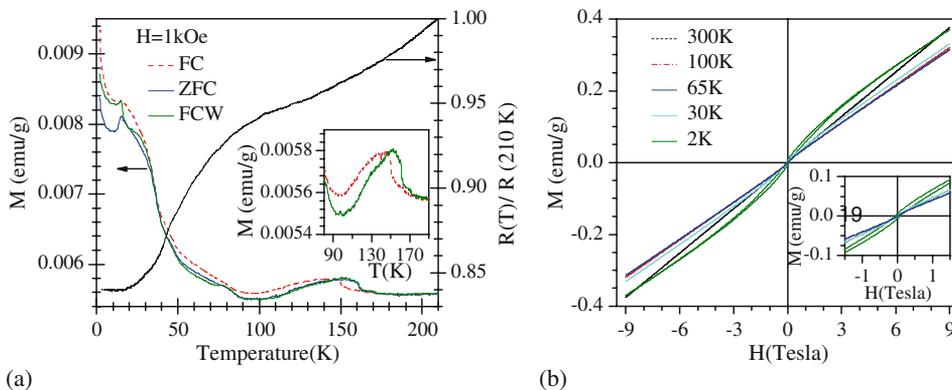


Figure 9. (a) Variation of magnetization with zero-field-cooled (ZFC), field-cooled (FC) and normalized resistance ($R(T)/R(210\text{ K})$) as a function of temperature for CaFe_2As_2 . Inset shows magnified view of anomaly in magnetization with field cooling (FC) and warming (FCW) cycles respectively. Variation of magnetization as a function of magnetic field at selected temperatures is shown in (b). Inset shows magnified view of the same.

at 2 K and not at any other temperature. M vs. H data do not show saturation at any temperature even at fields as high as 9 T. This clearly indicates that the compound is predominantly antiferromagnetic as evidenced in neutron diffraction, and small hysteresis at 2 K probably is indicative of additional weak ferromagnetism at the lowest temperature. There could be several possibilities for this weak ferromagnetism. Presence of small Fe impurity can be ruled out, as no evidence was seen in our neutron diffraction. Further, no magnetic saturation as was seen in ref. [12], not even technical saturation was observed in the present case. The paramagnetic Curie–Weiss-like magnetic contribution below ~ 160 K can come from the residual tetragonal phase which is present down to the lowest temperature and might have the tendency to order at low temperatures. Alternatively, AFM moments can have slight canting which is small enough to be undetected in neutron but large enough to be picked up in magnetization. The exact origin of weak ferromagnetism cannot be conclusively pin-pointed in the present case, which is anyway not the focus of this work.

The variation of $R(T)/R(210\text{ K})$ with temperature also shows a change in the slope around the same temperature. Also a finite resistivity is seen even at very low temperatures (up to 3 K) clearly ruling out superconductivity in this compound at ambient pressures. A range of magnetic phase transition temperatures can be found in literatures, which are strongly dependent on preparation and annealing conditions of the samples [33,39,40]. It is known that crystals grown out of FeAs self-flux show significantly different physical properties compared to crystals grown out of Sn flux [33,40b]. The smearing of anomaly in polycrystalline sample is very similar to the behaviour observed in the $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, and $(\text{Ca}_{1-x}\text{Na}_x)\text{Fe}_2\text{As}_2$ systems [41,42]. Thus, the large changes in the physical properties could be a result of variation of preparation conditions of the present sample. We have measured magnetization vs. magnetic field isotherms at different temperatures as shown in the lower panel of figure 9b. Presence of a small hysteresis loop in magnetization vs. magnetic field data at 2 K is a signature for weak ferromagnetism. However, we have not observed hysteresis loops at other temperatures.

The structural and magnetic phase transitions in the parent AFe_2As_2 (122 family) compounds are concomitant in temperature. However, the nature of the phase transition varies in different compounds. For BaFe_2As_2 , some groups have argued that the structural and magnetic transitions are second-order by showing that the transition is continuous, while first-order behaviour such as a large hysteresis has been observed by other groups [43,44] and found to be dependent on sample preparation method.

Recently, Saparov *et al* [40] reported that CaFe_2As_2 exhibits complex structure depending on annealing and preparation conditions. The authors have argued that quenching of the crystals from high temperature gives static random displacements of the atoms from their equilibrium positions leading to strained states. As a consequence of the non-uniform strain distribution in the sample it can be inhomogeneous. Ran *et al* [33] argued that quenching of large crystals from the flux essentially locks in the excess As and Fe, which determine the amount of strain in the sample. Thus, the observed behaviour in the physical properties and phase transition behaviour of CaFe_2As_2 in the present study could be a result of variation in preparation and annealing conditions.

To understand the origin of the phase transition in these materials, extensive theoretical studies have been performed by various researchers [8,28,31,32]. Theoretical calculations on CaFe_2As_2 have shown that the orthorhombic phase has higher volume

compared to the tetragonal phase. This is in agreement with our diffraction data. Further, the total energy difference between the orthorhombic and the tetragonal phases is ≈ 1 meV/degree of freedom and such a small difference in total energy suggests that energetically both phases could be stabilized at finite temperatures, thus giving the possibility for the coexistence of both phases. Our experimental observations are consistent with this picture.

4. Conclusion

In summary, the thermal expansivities and phase stability of AFe_2As_2 ($A = Ca, Sr$ and Eu) have been investigated by powder diffraction techniques in the temperature range 5–600 K. We found anisotropic thermal expansivities with temperature for all the compounds. The lattice parameter in the tetragonal phase (A_T) of $CaFe_2As_2$ contracts with increasing temperature, whereas C_T expands. The rate of contraction in A_T is lower than the rate of expansion in C_T . Other compounds show normal thermal expansion behaviour along both the a - and c -axes. In-plane expansion (i.e. along a -axis) is found to be the smallest for $EuFe_2As_2$ and the highest for $BaFe_2As_2$. However, the rate of change of thermal expansivities out-of-plane (i.e. along the c -axis) is higher as we go from compounds of Ba, Sr, Eu to Ca. We have also observed experimental evidence for the phase coexistence in polycrystalline $CaFe_2As_2$ in contrast with other 122 compounds studied. The orthorhombic phase has higher unit cell volume compared to that of the tetragonal phase. We have found that the magnetic structure determined by us for the orthorhombic phase is consistent with the literature. Diffraction data do not indicate the coexistence of phases over a wide range of temperature in $SrFe_2As_2$ and $EuFe_2As_2$ compounds unlike in the $CaFe_2As_2$ compound.

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