Formation of collapsed tetragonal phase in EuCo$_2$As$_2$ under high pressure

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Abstract
The structural properties of EuCo$_2$As$_2$ have been studied up to 35 GPa, through the use of x-ray diffraction in a diamond anvil cell at a synchrotron source. At ambient conditions, EuCo$_2$As$_2$ ($I4/mmm$) has a tetragonal lattice structure with a bulk modulus of 48 $\pm$ 4 GPa. With the application of pressure, the $a$ axis exhibits negative compressibility with a concurrent sharp decrease in $c$-axis length. The anomalous compressibility of the $a$ axis continues until 4.7 GPa, at which point the structure undergoes a second-order phase transition to a collapsed tetragonal (CT) state with a bulk modulus of 111 $\pm$ 2 GPa. We found a strong correlation between the ambient pressure volume of 122 parents of superconductors and the corresponding tetragonal to collapsed tetragonal phase transition pressures.

1. Introduction
In recent years, there has been continued interest in using the pressure as a variable in the study and discovery of superconducting properties, and magnetic and structural phase transitions in materials. Among such materials studied are the pnictides AFe$_2$As$_2$ ($A =$ divalent alkaline earth metal or divalent rare-earth metal). These form in the tetragonal ThCr$_2$Si$_2$ (‘122’) type structure and can exhibit superconductivity under chemical doping (isoelectronic or electron) and the application of external pressure [1–5]. The Fe atom can be replaced by Co and the As atom can be replaced by the isoelectronic element P forming ternary phosphides in the same 122-type structure [6]. Studies on 122 phosphate systems have been carried out and isostructural transitions from tetragonal to collapsed tetragonal accompanied by negative compressibility axial properties have been reported in ternary phosphides under pressure [7, 8] and in other compounds [9]. It has been observed that the transition metal element essentially determines the nature of this phase transition in ternary phosphides. For instance, compounds such as EuFe$_2$P$_2$ exhibit a second-order phase transition under pressure: however, in contrast to EuFe$_2$P$_2$, the pressure-induced structural phase transition is first order in compounds such as EuCo$_2$P$_2$ in which the Fe atom is replaced by a Co atom [7, 8]. These experimental findings lead one to wonder whether the type of transition metal ($T =$ Fe, Co) determines the first-order or second-order nature of tetragonal to collapsed tetragonal phase transitions in all 122-type compounds. Increasing interest in studying the compression behavior of the AFe$_2$As$_2$ family has been generated by the recent discovery of superconductivity and also the pressure-induced isostructural (tetragonal to collapsed tetragonal) phase transition accompanied by extremely anisotropic and negative compressibility axial phenomena in which the $a$-axis length increases while the $c$-axis length decreases under pressure in the ternary iron pnictide superconductors EuFe$_2$As$_2$ [10], BaFe$_2$As$_2$ and CaFe$_2$As$_2$ [11]. The negative compressibility phenomenon is suggested to be a common phenomenon in other iron-based superconductors of type AT$_2$As$_2$ ($A =$ Ba, Eu, Sr, Ca and $T =$ Fe, Co). In order to investigate the structural properties of EuCo$_2$As$_2$, we have synthesized and performed measurements of the lattice parameters as a function of pressure at room temperature using the synchrotron x-ray diffraction technique. We have been motivated by the occurrence of the CT phase and the exotic negative compressibility phenomenon in isostructural compounds of ThCr$_2$Si$_2$ type.

2. Experimental details
Single-crystal samples of EuCo$_2$As$_2$ were grown from a CoAs flux, similar to that described in [2]. The crystals were ground
into a polycrystalline sample and loaded into a 60 μm hole in a spring-steel gasket that was first pre-indentend to ~50 μm thickness and mounted in a diamond anvil cell for high pressure x-ray diffraction experiments. In this study, no pressure medium was employed and hence the structural transition reported in this study corresponds to a non-hydrostatic case.

The high pressure x-ray diffraction experiments were carried out at the beamline 16-ID-B, HPCAT, Advanced Photon Source, Argonne National Laboratory. An angle dispersive technique with an MAR345 image-plate area detector was employed using a focused monochromatic beam with x-ray wavelength, \( \lambda = 0.4325 \) Å. Experimental geometric constraints and the sample-to-image-plate-detector distance were calibrated using a CeO\(_2\) diffraction pattern and were held at the standard throughout the entirety of the experiment. Pressure was applied through the use of a diamond anvil cell and an internal copper pressure standard placed next to the sample was employed for the calibration of pressure [12]. The Birch–Murnaghan equation [13] as shown by equation (1) was fitted to the available equation of state data on the copper pressure standard [12]:

\[
P = 3B_0 f_E (1 + 2f_E) \left\{ \frac{1}{2} + \frac{1}{2} (B' - 4) f_E \right\}
\]  

where \( B_0 \) is the bulk modulus, \( B' \) is the first derivative of the bulk modulus at ambient pressure and \( V_0 \) is the ambient pressure volume. The fitted values for the copper pressure standard are \( B_0 = 121.6 \text{ GPa}, B' = 5.583 \text{ and } V_0 = 11.802 \text{ Å}^3/\text{atom} \). The parameter \( f_E \) is related to volume compression and is described below:

\[
f_E = \frac{(1 + \frac{V}{V_0})^{2/3} - 1}{2}.
\]  

3. Results and discussions

The diffraction images obtained were integrated using the program FIT2D [14] to yield intensity versus diffraction angle (2\( \theta \)) plots. At ambient temperature and pressure, x-ray diffraction revealed a tetragonal structure with the lattice parameters \( a = 3.9752 \pm 0.0031 \) Å, \( c = 11.1011 \pm 0.0032 \) Å and an axial ratio \( c/a = 2.7926 \pm 0.0032 \) Å. These lattice parameters were confirmed independently through a collection of data using a PANanalytical X’Pert Pro MPD at room temperature (using Cu Kα1 radiation) and a LeBail fit giving \( a = 3.9671(1) \) Å and \( c = 11.0632(5) \) Å. The ThCr\(_2\)Si\(_2\)-type structure has the following crystalline arrangement: Eu atoms at the 2a position (0, 0, 0), Co atoms at the 4d positions (0, 1/2, 1/4) and (1/2, 0, 1/4), and As atoms at the 4e positions (0, 0, z) and (0, 0, -z). The approximate structural parameter \( z = 0.36 \) has been obtained based on Rietveld refinement of the x-ray diffraction data [15].

Figure 1(a) shows the x-ray diffraction pattern at 0.33 GPa with the EuCo\(_2\)As\(_2\) sample in the 14/mmm tetragonal structure and the copper pressure marker in the face centered cubic (fcc) phase. The diffraction peaks are labeled with their respective (hkl) values. The tetragonal phase of EuCo\(_2\)As\(_2\) is characterized by the (101), (110), (112), (200), (213) and (224) Bragg diffraction peaks. The fcc phase of the copper pressure marker is characterized by the (111), (200), (220), (311) and (222) Bragg diffraction peaks. The measured volume of the copper pressure marker obtained from x-ray diffraction was used to calculate the sample pressure from the equation of state given by equation (1). The obtained lattice parameters for the sample at a pressure of 0.33 GPa are \( a = 3.9923 \pm 0.0031 \) Å and \( c = 10.7347 \pm 0.01 \) Å. Figure 1(b) shows the x-ray diffraction pattern of the sample at 3.2 GPa with the lattice parameters \( a = 4.0114 \pm 0.0031 \) Å and \( c = 10.0698 \pm 0.0194 \) Å. When comparing the low pressure spectrum figure 1(a) with (b), the sample peaks are dependent only on the \( a \) axis: (110) and (200) are all moving to lower diffraction angles while all non-\( a \)-dependent peaks move to higher diffraction angles and peaks dependent on both \( a \) and \( c \) remain approximately in the same position. Conventional behavior of the material under compression suggests that all peaks would move to higher angles in the x-ray diffraction spectrum; however, in comparing figure 1(a) with (b) all \( a \)-dependent peaks move to lower diffraction angles. This is a clear indication of negative compressibility in the \( a \) axis of the tetragonal lattice structure in EuCo\(_2\)As\(_2\) due to the increase in the \( a \) axis concurrent with a sharp decrease in the \( c \) axis with the application of pressure. Similar observations were seen in EuFe\(_2\)As\(_2\) [10] BaFe\(_2\)As\(_2\) and CaFe\(_2\)As\(_2\) [11] during the transition to their respective collapsed tetragonal phases under compression. Another important note is that the predominant peaks unlabeled in the diffraction spectra in figure 1 are identified as the CoAs orthorhombic impurity phase (Cmcm) flux, which might have remained on the surface of the crystals. These peaks are predominant in the spectrum below 13 GPa and become progressively less evident at higher pressures.
The decompression of the sample from high pressure exhibiting a normal compression behavior beyond and up to compressibility effects reaching a maximum at about 3.2 GPa and then decompressed, exhibiting normal behavior up to 14 GPa increasing pressure up to 3.2 GPa prior to exhibiting normal behavior up to 14 GPa increasing pressure up to a pressure of 35.8 GPa. The sample was then decompressed, exhibiting normal behavior up to 14 GPa where a hysteresis occurs. The \( a \) axis begins to increase at a more rapid rate, reaching a maximum at 5.1 GPa prior to returning to slightly below its initial value. The anomalous behavior of the \( a \) axis is paired with a sharp but continuous decrease in \( c \) axis until 4.7 GPa, where a normal decrease in lattice parameter length occurs up to 35.8 GPa where, upon decompression, the \( c \) axis returned to approximately its initial length.

Figure 2 shows the measured \( a \) axis as a function of pressure, exhibiting an anomalous compression phenomenon. The \( a \) axis shows an initial increase in axial length with increasing pressure up to 3.2 GPa prior to exhibiting normal compression up to a pressure of 35.8 GPa. The sample was then decompressed, exhibiting normal behavior up to 14 GPa where a hysteresis occurs. The \( a \) axis begins to increase at a more rapid rate, reaching a maximum at 5.1 GPa prior to returning to slightly below its initial value. The anomalous behavior of the \( a \) axis is paired with a sharp but continuous decrease in \( c \) axis until 4.7 GPa, where a normal decrease in lattice parameter length occurs up to 35.8 GPa where, upon decompression, the \( c \) axis returned to approximately its initial length.

Figure 3 shows all the axial ratio \( (c/a) \) data points that were obtained during this experiment and we have combined the data obtained during compression and decompression into one dataset for subsequent analysis. The axial ratio shows a sharp decrease with increasing pressure up to 4.7 GPa and then a gradual decrease with further increase in pressure up to the highest pressure of 35.8 GPa. The variation of \( c/a \) with pressure can be divided into two linear regions. The fits for the two linear regions are shown in figure 3 and are described by the following equations:

\[
\frac{c}{a} = 2.7102 - 0.53 P, \quad 0 \text{ GPa} \leq P \leq 4.7 \text{ GPa}, \tag{3}
\]

\[
\frac{c}{a} = 2.4762 - 0.001 P, \quad 0 \text{ GPa} \leq P \leq 35.8 \text{ GPa}. \tag{4}
\]

The intersection of the two linear regions as described by equations (3) and (4) defines the phase transition from the ambient pressure T phase to the CT phase. \( \text{EuCo}_2\text{As}_2 \) is found to undergo this phase transition at 4.7 GPa at ambient temperature. The nature of this phase transition is clearly continuous, as can be seen in the pressure dependence of the structural parameters (figures 2–4). A similar continuous T to CT phase transition has been observed in the compression behavior of the related ThCr\(_2\)Si\(_2\) structure-type compounds of EuFe\(_2\)As\(_2\) [10], EuFe\(_2\)P\(_2\) and LaFe\(_2\)P\(_2\) [5–7]. This is in sharp contrast to observations made in ternary phosphides in which replacing Fe atoms with Co atoms reduces the nature of the observed structural phase transition from second-order (continuous) to first-order (discontinuous) type [7, 8]. The bonding characteristics of As and P atoms along with the pressure-induced changes in electronic structure determine the formation of the collapsed tetragonal structure in these materials. An additional consideration for present studies is that the high pressure Mössbauer investigations on EuFe\(_2\)P\(_2\) have revealed a continuous structural phase transition which is accompanied by a continuous valence transition from a magnetic Eu\(^{2+}\) state to a nonmagnetic Eu\(^{3+}\) state in the pressure range between 3 and 9 GPa [16]. We expect this valence fluctuation to have an influence on magnetic phase transitions at low temperatures and have an overall effect on structural phase transitions under high pressure at room temperature due to enhanced compressibility that accompanies valence fluctuations.

Figure 4 shows the measured pressure–volume curve of \( \text{EuCo}_2\text{As}_2 \) up to 35.8 GPa at ambient temperature. The pressure–volume data were fitted by the Birch–Murnaghan equation of state described by equation (1). The fits from the axial ratio showed a phase transition from the T to the CT phase at 4.7 GPa. The transition pressure obtained from the axial ratio was used to separate the tetragonal phase from the collapsed tetragonal phase when determining the equation of state for \( \text{EuCo}_2\text{As}_2 \). The fitted zero-pressure volumes \( (V_0) \)
the two phases occurs at 4.7 GPa.

The Birch–Murnaghan equation of state fitted to the two phases, i.e. the tetragonal (T) phase and the collapsed tetragonal (CT) phase. The fitted parameters are summarized in table 1. The transition between the two phases occurs at 4.7 GPa.

Table 1. Equation of state parameters for EuCo2As2 in tetragonal (T) phase and collapsed tetragonal (CT) phase at ambient temperatures.

| Phase            | Unit cell volume ($V_0$) at ambient conditions | Bulk modulus ($B_0$) | Pressure derivative of bulk modulus ($B’$) |
|------------------|-----------------------------------------------|----------------------|-------------------------------------------|
| Tetragonal (T)   | 172.4 ± 0.7 Å³                                  | 48 ± 4 GPa           | 4 (assumed)                               |
| Collapsed tetragonal (CT) | 165.9 ± 0.3 Å³                                  | 111 ± 2 GPa          | 3.06                                      |

for the tetragonal and collapsed tetragonal phases are 172.4 ± 0.7 Å³ and 165.9 ± 0.3 Å³, respectively. The measured change in volume with the application of pressure shows a significant decrease in overall unit cell volume, indicating the collapsed tetragonal phase has a 3.8% higher density than the tetragonal phase at zero pressure. The Birch–Murnaghan fit revealed a bulk modulus for the tetragonal phase to be $B_0 = 48 ± 4$ GPa and $111 ± 2$ GPa for the CT phase. This comparison shows that the T phase is 2.3 times more compressible than the CT phase at zero pressure. Due to the limited number of data points in the tetragonal phase, the first derivative of the bulk modulus could not be estimated and was fixed at four. The calculated first derivative of the bulk modulus for the collapsed tetragonal phase was found to be $B’ = 3.06$. These fitted parameters are summarized in table 1.

Figure 5 shows the correlation between the observed zero-pressure volume ($V_0$) for AT2As2 122 materials (A = Ba, Fe, Ca and Eu; T = Fe, Co) and their corresponding phase transition pressures ($P_T$) from T to CT phases at 300 K. The data for EuFe2As2 were obtained from [10] and the data for CaFe2As2 were taken from [11]. The variation shows a nearly linear increase in $P_T$ with increasing $V_0$. The solid curve is the linear fit to data and is described by the equation below:

$$P_T = 0.388V_0(±0.034)$ GPa Å$^{-3} − 63.259(±6.2)$ GPa. (5)

Following this work, we suggest that the transition from the T to the CT phase, under compression with a concurrent negative axial compressibility, is a common effect in all the parents of iron-based arsenic 122 superconductors and perhaps other related compounds of the 122-type. The T to CT phase of these compounds at 300 K can be estimated using equation (5) if their corresponding zero-pressure volume at ambient temperature is known. The pressure-induced isostructural phase transition to a collapsed tetragonal at ambient temperature is not unique among arsenic compounds that have ThCr2Si2-type structure. The effect is found among the phosphides that are isostructural to AT2As2 compounds such as EuCo2P2, SrNi2P2 [7] and EuFe2P2 [16]. These phosphides compounds have been widely studied and the rapid decrease observed in their $c/a$ ratios in the collapsed tetragonal phase has been attributed to bonding transitions associated with the formation of a P–P single bond between ions in adjacent planes along the c axis [17]. In connection to arsenic compounds, recent theoretical calculations for CaFe2As2 suggest that there is a similar transition in the bonding character of As ions and the enhancement of the As–As bonds across the Fe2As2 layers under pressure [18]. This work and previous studies on the related 122 compounds suggest that the collapsed tetragonal phase, with the space group. $I4/mmm$, is the stable high pressure phase of the AT2As2-type compounds, and there has been no evidence of post-collapse phase transitions at least up to the maximum pressures of these studies (70 GPa in EuFe2As2 [10], 56 GPa in BaFe2As2, 51 GPa in CaFe2As2 [11] and 35 GPa EuCo2As2).
4. Conclusions

In summary, we have studied the pressure effects on the crystal structure of the layered ThCr$_2$Si$_2$-type EuCo$_2$As$_2$ up to 35.8 GPa at ambient temperature using synchrotron x-ray diffraction. The x-ray diffraction patterns collected reveal a highly anisotropic and anomalous compressibility effects in which the $a$ axis increases with increasing pressures up to a maximum then decreases normally while the $c$ axis decreases continuously with increasing pressure. Analysis of the x-ray diffraction data indicates a tetragonal phase to a collapsed tetragonal phase transition in EuCo$_2$As$_2$ at 4.7 GPa. The equations of state for the T and CT phases show distinct bulk moduli. At ambient pressure, an extrapolated CT phase has a density that is 3.8% higher as compared to the T phase under similar conditions. We suggest that the transition from the T to CT phase under compression, along with a concurrent negative axial compressibility, is a common effect in every compound of the type AT$_2$As$_2$ (A = Ba, Ca, Sr, Eu and T = Fe, Co). A linear correlation between the ambient pressure volume for such 122 materials and their corresponding phase transition pressures from the T to CT phase at 300 K is obtained. Additional systematic theoretical and experimental studies of structural phase transitions in AT$_2$As$_2$ compounds under hydrostatic and non-hydrostatic pressure conditions are required to clearly establish a correlation between transition pressure, initial volume and electronic structure of these materials.

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