Superelasticity and cryogenic linear shape memory effects of CaFe$_2$As$_2$

John T. Sypek$^1$, Hang Yu$^2$, Keith J. Dusoe$^1$, Gil Drachuck$^3$, Hetal Patel$^1$, Amanda M. Giroux$^1$, Alan I. Goldman$^3$, Andreas Kreyssig$^3$, Paul C. Canfield$^3$, Sergey L. Bud’ko$^3$, Christopher R. Weinberger$^{2,4}$ & Seok-Woo Lee$^1$

Shape memory materials have the ability to recover their original shape after a significant amount of deformation when they are subjected to certain stimuli, for instance, heat or magnetic fields. However, their performance is often limited by the energetics and geometry of the martensitic-austenitic phase transformation. Here, we report a unique shape memory behavior in CaFe$_2$As$_2$, which exhibits superelasticity with over 13% recoverable strain, over 3 GPa yield strength, repeatable stress-strain response even at the micrometer scale, and cryogenic linear shape memory effects near 50 K. These properties are achieved through a reversible uni-axial phase transformation mechanism, the tetragonal/orthorhombic-to-collapsed-tetragonal phase transformation. Our results offer the possibility of developing cryogenic linear actuation technologies with a high precision and high actuation power per unit volume for deep space exploration, and more broadly, suggest a mechanistic path to a class of shape memory materials, ThCr$_2$Si$_2$-structured intermetallic compounds.
Materials, when subjected to external loads, deform either elastically or plasticity. If the deformation is elastic, the material can easily recover its shape when the external stimuli is removed since shape change is governed by the reversible stretching of atomic bonds, which simply relax with the removal of the load. However, it is often the case that material shape cannot be recovered easily, as the deformation is plastic and usually involves the rearrangement of bonds in addition to simple bond stretching. There is one unique case in which the shape of a material can be significantly changed and a large amount of deformation can remain, but can be restored through a reversible phase transformation that is induced through additional stimuli such as a change in temperature and the application of magnetic fields. This type of material is called a shape memory material (SMM). Because the reversible phase transformation usually brings about a large structural recovery, it is often possible to obtain high recoverable strains, an effect that is called superelasticity or pseudo-elasticity. Superalastic performance of SMMs is usually determined by total work (spring-back) release per unit volume, which corresponds to the maximum possible work done by SMMs. This maximum work release can be calculated by measuring the area below stress–strain curve between zero strain and the elastic limit. The actuation performance of SMMs is usually determined by the actuation work per unit volume, which is the area below a stress–strain curve within phase transformation strain. Note that the total work release is different from the actuation work because the total work release considers the total recoverable strain, but the actuation work considers only the phase transformation strain. Most crystalline shape memory metallic alloys exhibit superelasticity through a martensitic-austenitic phase transformation, which is a shear process and can produce, in general, recoverable strains up to 10%–68 with only a few exceptions, but yield strengths are typically much lower than 1 GPa. Of particular note, single crystalline-shape memory ceramic micropillars exhibit a maximum elastic limit of ~10% and a maximum yield strength of ~2.5 GPa, both of which lead to a high work release per unit volume. Also, their high actuation stress (1–2 GPa) and high actuation strain (~10%) produces ultra-high actuation work per unit volume (~50 MJ/m³). In terms of work release and actuation work per unit volume, shape memory ceramic micropillars are currently regarded as the state-of-the-art SMMs. This leads us to a fundamental materials science research that asks us to search for any other crystalline material systems to exhibit superelastic and actuation performances comparable or even better than shape memory ceramic micropillars. Given that superelasticity and shape memory effects are primarily the result of the atomic bond strength and the geometric relationship between martensite and austenite phases, new materials that potentially have strong atomic bonds and new phase change mechanisms must be found in order to obtain excellent superelastic and actuation performances. Therefore, we turn our attention to novel intermetallic compounds with competing electronic, magnetic, and structural transitions that are currently studied at the frontiers of material physics for properties such as superconductivity.

The ternary, intermetallic compound, CaFe₂As₂, which has been extensively studied as an Fe-based superconductor, has recently been found to exhibit remarkable pressure sensitivity of its crystal structure as well as its electronic/magnetic properties. As shown in Fig. 1a, this material undergoes phase transformation from the tetragonal to the collapsed tetragonal (cT) phase at room temperature for applied hydrostatic pressures just under 2 GPa and from an orthorhombic, anti-ferromagnetic phase to the cT phase below 50 K for pressures below 0.5 GPa. X-ray diffraction measurements have demonstrated that the abrupt reduction of lattice parameter along c axis during transformation to the cT phase correspond to an axial strain of ~10%. CaFe₂As₂ has been shown to be exceptionally pressure and stress sensitive; post crystal growth, annealing and quenching experiments on CaFe₂As₂ and its related structures (e.g., Ca(Fe₁₋ₓCoₓ)₂As₂) have revealed that it is possible to tune these phase transformations by controlling the internal strain associated with compositional fluctuation or nanoprecipitates, allowing the cT transition to even manifest at ambient pressures. Since the phase transformation strain is roughly 10%, it is possible to achieve total recoverable strains that exceed 10% if the material is elastically compliant enough to accommodate sufficient elastic strain as well as mechanically hard enough to suppress plasticity.

Results

Uni-axial compression on [001] CaFe₂As₂ micropillars. To test the hypothesis that these materials exhibit superior superelastic properties and even can be used as shape memory compounds, we investigated the mechanical response of a solution-grown, single crystal of CaFe₂As₂ using an in situ microcompression test in a scanning electron microscope (SEM) and in situ cryogenic neutron scattering test under pressure. We grew, out of a Sn rich quaternary melt, a millimeter-sized plate-like single crystal that possesses mirror-like (001) and [103] facets (Fig. 1b). Both hydrostatic pressure and thermal expansion studies suggest that the phase transformation occurs mainly due to a structural collapse along c axis of the tetragonal (or orthorhombic) lattice.

Thus, uni-axial compression tests along c axis would be the most straightforward way to characterize either superelastic, actuation, or potential shape memory properties. Due to the plate-like geometry and small dimensions of solution-grown single crystals, it is difficult to perform conventional, bulk-scale, uni-axial mechanical tests. In addition, the irregular shapes of these as-grown crystals would result in a non-uniform stress state during loading, which could lead to un-intended plastic deformation or fracture during mechanical testing. To mitigate these issues with conventional testing, we utilize the recently developed microcompression technique that uses a focused-ion beam to create cylindrical micropillars and a flat-end nanoindenter to compress the single crystal precisely along its c axis. Micropillars with 2 μm diameters were fabricated on the (001) surface of the single crystal, so that our micropillars are aligned along the c-axis of tetragonal lattice (Fig. 1c). Then, uni-axial compression tests were performed in SEM.

First, we compressed a single micropillar up to ~11.3% strain three times, and the stress–strain curves demonstrate recoverable and repeatable responses for each cycle (Fig. 2a). The SEM images before and after three cycles of compression revealed no difference in height (the inset of Fig. 2a). Thus, this large amount of deformation is fully recovered. Also, the repeatable nature of
the stress–strain response implies that there is no residual damage or evidence of a stochastic transformation. This behavior is similar with that of NiTiHf shape memory alloys that exhibit an excellent repeatability with a negligible amount of fatigue damage21. We also performed cyclic tests with ~10% strain and 100 cycles, and confirmed that this large deformation is fully recoverable and repeatable even after 100 cycles (Supplementary Fig. 1 and Supplementary Note 1). Note that the shape of micropillar in the inset of Fig. 2a is obscured due to the ring around a micropillar. At the final stage of focused-ion beam milling, we use a thin co-centric circular pattern that, when is sometimes insufficiently wide, leaves a ring of material behind. Because the focused-ion beam is highly uniform over the pattern, however, the shape of micropillar is nearly symmetric, and the ring is not attached to a micropillar. We used the height of the right side of the micropillar, which is clearly visible, and also further confirmed that the stress–strain curves in Fig. 2a overlaps the stress–strain curve in Fig. 2c, which was measured from the symmetric micropillar in Fig. 1c (before compression) and the inset of Fig. 2c (after compression). Also, we always carefully inspect the measured displacement from in situ deformation movies. Thus, all stress–strain data in this manuscript were correctly measured (Supplementary Fig. 2 and Supplementary Note 2). Additional stress–strain curves are also available in Supplementary Fig. 3, which confirm that our method produces reasonably consistent superelasticity results.

The stress–strain curves exhibit three distinct deformation behaviors (stage I, II, and III) (Fig. 2a). Note that the existence of

---

**Fig. 1** Intermetallic compound CaFe$_2$As$_2$. **a** The phase diagram of CaFe$_2$As$_2$ in temperature-pressure space (12). **b** An optical microscope image of solution-grown single crystalline CaFe$_2$As$_2$; scale bar, 1 mm. **c** A [001]-oriented CaFe$_2$As$_2$ micropillar with 2 μm in diameter made by Ga + focused-ion beam milling; scale bar, 1 μm.
non-linear behavior (stage II) resembles that of typical SMMs, which corresponds to a phase transformation. Another feature that is notable in the stress–strain curves is the relative narrowness of the hysteresis loop, which is also quantitatively different from standard SMMs that exhibit substantially larger hysteresis loops at room temperature. Thus, CaFe\(_2\)As\(_2\) would be able to release the large amount of work without significant damping effects. Most crystalline SMMs exhibit a non-linear response through the martensitic–austenitic phase transformation. Because this shear transformation almost always produces a localized shear strain on the micrometer scale, a kinked shape is easily observed during compression on a single crystalline micropillar of conventional shape memory materials. For CaFe\(_2\)As\(_2\), however, we confirmed via our in situ mechanical test of various micropillars observed along different viewpoints and at a high magnification (up to 7000×) that CaFe\(_2\)As\(_2\) always shows only a height reduction along the c axis (loading direction) without any lateral motion of the pillar, the formation of slip steps, or strain bursts. These results imply that phase transformation is not related to a shear process at all (Fig. 2a) but rather a simple reduction in lattice constant along the c axis that is expected for this compound undergoing a cT phase transition. Thus, superelasticity in CaFe\(_2\)As\(_2\) is exhibited by non-martensitic–austenitic phase transformation. In our experiment, shear-like phenomena are only observed in conjunction with plastic yielding (see the formation of shear slip steps in the inset of Fig. 2c).

For CaFe\(_2\)As\(_2\), we confirmed that as long as the micropillar diameter is large enough to neglect the FIB effect damage layer (typically, pillar diameter >1 μm), CaFe\(_2\)As\(_2\) micropillars exhibit no size dependence in stress–strain curve. This would be because the unit length scale of the phase transition is only the dimension of the unit cell, which is far smaller than the micropillar diameter.

**Fig. 2** Demonstration of superelasticity including large recoverable strains and high yield strengths. a A three stress–strain curves of same [001]-oriented CaFe\(_2\)As\(_2\) micropillar; the inset shows no height change even after three cycles of 11.3% strain compression. Remarkably, the stress–strain curves appear identical, indicating that there is no residual damage accumulation during cyclic deformation, which is typically observed in shape memory alloys or ceramics especially at small length scales. Stress–strain data of Ni-Ti alloy also was included for comparison. Two snapshots of in situ compression show the significant compressive elastic deformation, which cannot be achieved in other metallic or intermetallic materials; scale bar, 1 μm. b Electron density distributions at ambient pressure and under c-axis compression; the formation of As–As bonding, which is indicated by arrows, induces the structural collapse and the 10% height reduction. The iso-surface level used was 0.035 and the max is 0.1 (red). c Experimental and computational (DFT) stress–strain curves of [001]-oriented CaFe\(_2\)As\(_2\) micropillar up to the yield point. We intentionally terminated the stress–strain data of DFT simulation at the experimental yield strength because the remaining data above the yield strength is not meaningful in the current analysis. The inset shows the plastic slip in the [30\(\bar{1}\)](103) slip system.
Density functional theory calculations on superelasticity. In order to provide additional insight into the unusual form of superelasticity in CaFe$_2$As$_2$, we performed the density functional theory (DFT) simulations of the compression process. Since DFT calculations are done at 0 K, the stable phase of CaFe$_2$As$_2$ predicted is the anti-ferromagnetic orthorhombic phase, which is different from the paramagnetic tetragonal phase of our room temperature experiments. As revealed previous work on the different from the paramagnetic tetragonal phase of our room temperature experiments, noted is the anti-ferromagnetic orthorhombic phase, which is expected in the real material. To simulate this realistic case, we use a composite model that minimizes the total enthalpy under load control, similar to the experiments, to determine the phase fractions of the orthorhombic and cT phases via minimization (Supplementary Figs. 5, 6, 7 and Supplementary Note 3). The resulting stress-strain curve is shown in Fig. 2c. DFT simulations, in conjunction with a simple analytical model, demonstrate that in the course of compression, the partial phase transformation is energetically more favorable than the full/abrupt transformation of the entire volume of specimen. Thus, the volume fraction of cT phase gradually increases in the course of deformation, leading to continuous stress-strain curve in Fig. 2c. The unit cell still undergoes the abrupt structural collapse locally, but the macroscopic response of micropillar exhibits the gradual and continuous deformation. Note that the transition to the cT phase is not associated with an invariant plane as is common in traditional shape memory materials, which is an un-distorted and un-rotated plane, in the strictest sense. This is because there is a small in-plane strain on the (001) plane during the phase transition (Fig. 2b). However, this strain is small making this plane the most favorable interface between the two phases. The details of microstructural evolution could be confirmed by by performing in situ electron back-scattered diffraction (EBSD) or in situ transmission electron microscope (TEM) micropillar compression test.

Despite the large number of assumptions in our model, it clearly captures all phases of deformation including the smooth stage II transition from orthorhombic to cT phase. Indeed, the formation of As–As bonding (phase transformation) is the major process that induces the non-linearity of stress–strain curve. Note that superelasticity mechanism in CaFe$_2$As$_2$ is unique because it is not exhibited by the martensite-austenite phase transformation of conventional shape memory alloys and ceramics. From these single unit cell and composite simulations, it is clear that the large values of recoverable strain observed in CaFe$_2$As$_2$ occur by the combination of linear elastic strain, hyperelastic strain, and phase transformation strain.

Superelasticity and actuation performances. It is clear from our experiments that we have yet to observe the maximum recoverable strain, the yield strength, the maximum work release per unit volume, and the actuation work per unit volume of this material. To determine these values in compression, we performed an additional micropillar compression test, increasing stress until we see either plastic deformation or fracture, and determined that the elastic limit is ~13.4 % and the yield stress is ~3.7 GPa, both of which is even higher than those of single crystalline shape memory ceramic micropillars, which have been known to possess the current state-of-the-art superelastic work and actuation work per unit volume (Figs. 2c and 3). Returning to the composite material model we see that at the experimentally determined yield stress, the simulation suggests ~13% recoverable strain, which agrees well with our experimental results. Intermetallic compounds typically possess strong directional atomic bonds, which explain why the strength is much higher than shape memory alloys or even shape memory ceramics. In fact, the strong directional bonds help suppress plastic deformation in CaFe$_2$As$_2$, increasing the recoverable strain from roughly ~7% associated with the phase change to ~13.4% which includes elastic strain.

The combination of the high recoverable strains (13.4%) and high yield strengths (3.7 GPa) are even higher than those of shape memory ceramic micropillars. Also, long hysteresis area allows CaFe$_2$As$_2$ to absorb and release ultra-high work per unit volume with minimal dissipation at room temperature. The stress–strain curves in Fig. 2a suggest that the energy loss by damping is about 10% based on the ratio of the areas under the loading-to-unloading curves. Assuming that this percent loss is similar up to elastic limit, we can estimate the maximum possible work absorption/release per unit volume by using 90% of the area under the stress–strain curves between zero strain and the elastic limit in Fig. 2c; this corresponds to $1.76 \times 10^8$ J/m$^3$ (experiment) and $1.57 \times 10^8$ J/m$^3$ (DFT) for the absorption of, and $1.58 \times 10^8$ J/m$^3$ (experiment) and $1.40 \times 10^8$ J/m$^3$ (DFT) for the release of work per unit volume (for 10% of damping effect). These results imply that CaFe$_2$As$_2$ is able to release the superelastic work about...
10-1000 times larger than most engineering materials (e.g., stainless steel: 10^7 J/m^3, Zr-based bulk metallic glass: 2 x 10^7 J/m^3, shape memory ceramic micropillars: 4 x 10^7 J/m^3; shape memory alloys: 10^8 J/m^3). Some shape memory metallic alloys could show the larger recoverable strain. Due to their low yield strength and high damping effect, however, their work release per unit volume (~10^8 J/m^3) is much lower than CaFe_2As_2 (1.76 x 10^9 J/m^3). Furthermore, as noted before, the actuation capability is determined by the maximum possible actuation work per unit volume which is the area below a stress-strain curve within phase transformation strain range (the gray trapezoidal area in Fig. 2c), which corresponds to ~ 5.15 x 10^7 J/m^3. This can be estimated by multiplying the actuation strain by the average actuation stress (\(\sigma_{\text{ave}}\)), which is the average of the onset (\(\sigma_{\text{onset}}\)) and offset (\(\sigma_{\text{offset}}\)) phase transformation stresses (Fig. 2c). On the basis of this scheme, we can compare the actuation capability of CaFe_2As_2 with other actuation systems by locating our four micropillar results and one DFT result with the actuation stress and the average actuation stress (Supplementary Fig. 8, Supplementary Table 1, and Supplementary Note 4). Fig. 3 shows a comparison of actuation capability, by plotting actuation stress vs. actuation strain, of CaFe_2As_2 compared with other actuation systems by locating our four micropillar results and one DFT result with the actuation stress and the average actuation stress (Supplementary Fig. 8, Supplementary Table 1, and Supplementary Note 4). Fig. 3 shows a comparison of actuation capability, by plotting actuation stress vs. actuation strain, of CaFe_2As_2 compared with other materials (Supplementary Table 1, and Supplementary Note 4).
actuation stress (see the gray colored stress–strain curve in Fig. 2a). As a special case, Norfleet et al. 28 investigated shape memory properties of Ni–Ti micropillars. Size effects can improve the phase transformation stress of Ni–Ti alloys, up to 800 MPa. Also, the transformation strain of Ni–Ti micropillar is around 0.06. Then, actuation work per unit volume of Ni–Ti micropillar (800 MPa × 0.06 = 4.8 × 10^7 J/m^3) is similar with that of CaFe₂As₂ (~5.15 × 10^7 J/m^3). Figure 3 clearly shows that CaFe₂As₂ shows the comparable actuation work per unit volume with shape memory ceramic micropillars (the current state-of-the-art) or the high-end of shape memory alloy. Thus, CaFe₂As₂ exhibit excellent actuation work per unit volume, compared to shape memory alloys.

Cryogenic linear shape memory behavior. The narrow hysteresis loop of CaFe₂As₂ would be associated with the different stress required to form and break the As–As bonds. This leads to the existence of hysteresis in stress–strain curve of CaFe₂As₂. Our DFT simulation results (Supplementary Fig. 4) and neutron scattering results by Goldman et al. 22 (Fig. 4a) show that CaFe₂As₂ exhibits the maximum width of hysteresis at 0 K. Without thermal vibrations, the As–As bonds are not broken even after the complete removal of compression stress. The neutron scattering experiment (Fig. 4a) show that a hydrostatic tensile load of 0.25 GPa (or ~0.25 GPa pressure) is required to destabilize cT phase at 0 K.22 As the temperature increases, thermal vibrations help the destabilization of the As–As bonds under some amount of compression stress (or pressure), leading to the narrower hysteresis. Figure 4a shows clearly that the width of hysteresis area becomes narrower as the temperature increases. Thus, increasing a temperature would be an effective way to make the hysteresis loop narrower and to maximize the release of mechanical work. Vice versa, it is possible to expect the cryogenic shape memory effects due to the metastability of cT phase at 0 K.

The DFT simulation of a single unit cell predicts that the cT phase is metastable after loading-unloading cycle at 0 K (Supplementary Fig. 4). In other words, cT phase is not transformed into orthorhombic phase even though the applied stress is completely removed at 0 K. However, our experimental data shows the full strain recovery at room temperature, suggesting that the cT phase is unstable at room temperature but may well be metastable near 0 K at atmospheric pressure. Metastability of cT phase is a pre-requisite to exhibit shape memory behavior. Thus, this work includes important evidence that, taken together with our current superelasticity results, suggests the existence of a cryogenic linear shape memory effect.

On the basis of this evidence, it is possible to suggest, two different deformation routes, path 1-2-3-4 and path 1′-2′, to demonstrate the cryogenic linear shape memory effects and thermal actuation, respectively (Fig. 4). In order to prove the existence of cryogenic shape memory effects, we conducted in situ cryogenic neutron scattering measurement on a single crystal of CaFe₂As₂ using a He gas pressure cell in a displacive cryogenic refrigerator. 22 In this experiment, it is possible to control both temperature and pressure and to check the occurrence of phase transformation at the same time (Fig. 4a). First, the temperature was decreased down to 50 K, and neutron scattering data clearly shows that the phase becomes orthorhombic (path 1 and Fig. 4b). Then, the pressure was increased until cT transition occurs (path 2 and Fig. 4b, c), and we confirmed that cT transition occurs between 350 and 400 MPa. A pre-requisite of the shape memory effect is metastability of the deformed state. To achieve this metastability of cT phase, we decreased the pressure down to 300 MPa (path 3), and neutron scattering data confirms that the transition to the T phase does not occur even below the critical pressure for the forward transition (350–400 MPa) (Fig. 4d). The transition to the O phase (at 50 K) only occurs when the pressure is decreased below 50 MPa (Fig. 4e). This clearly confirms that cT phase is metastable after path 3 and satisfies the pre-requisite of shape memory effect, which is metastable deformed state. After preparing the sample in the cT phase, within the hysteresis region, the temperature was increased from 50 to 100 K to destabilize the cT phase, and the transition to the orthorhombic phase occurs (path 4 in Fig. 4a, f). This is truly shape memory effect that exhibits the shape recovery by making the metastable deformed state unstable by applying the stimulus, heat (Fig. 4h). The transformation strain along a and b axes are much smaller than the transformation strain along c axis. Thus, the cT transition is nearly linear volume transformation (the volume changes only by the lattice expansion/contraction along c axis).

Discussion

The observation of superelastic and possible shape memory behavior in CaFe₂As₂ opens a number of possibilities because the phase transformation can be tuned by adjusting the chemical...
composition and by controlling the internal strain. For instance, the substitution of cobalt for iron coupled with annealing and quenching can induce the significant shift of boundaries in phase diagram in Fig. 1a. Thus, it is possible to tune the phase diagram to fit specific needs by engineering the chemistry as well as the microstructure of this class of materials. Furthermore, and perhaps of even greater importance, the cT phase transition found in CaFe$_2$As$_2$ is the only manifestation of a wider class of such transitions found in over 400 different ThCr$_2$Si$_2$-type intermetallic compounds. The novelty of this bond making/breaking phase transition was appreciated as early as 1985 when Hofmann and Zheng surveyed a number of potential systems that could manifest this type of transition. On the basis of our results on CaFe$_2$As$_2$, we fully anticipate that other members of the ThCr$_2$Si$_2$ structure class will manifest similar superelasticity and potential as SMM. Any ThCr$_2$Si$_2$-type intermetallic compounds that can undergo the cT transition under compression can exhibit superelasticity in the same way as long as they are not plasticity yielded or fracture before the phase transformation occurs. Some intermetallic compounds exist as a collapsed tetragonal state under stress-free condition. In this case, superelasticity can be shown under tension by breaking Si-Si type bonds, but the same transitions found in over 400 different ThCr$_2$Si$_2$-type intermetallic compounds that can correspond to the engineering strain rate of $0.002 \text{ s}^{-1}$. Any ThCr$_2$Si$_2$-type intermetallic compounds that can yield or fracture before the phase transformation occurs. Some intermetallic compounds exist as a collapsed tetragonal state under stress-free condition. In this case, superelasticity can be shown under tension by breaking Si-Si type bonds, but the same principle from our results works on this case, too. It is certainly beneficial to search for a new superelastic and shape memory materials that do not contain a toxic arsenic (As), which might make a poor impact to industry. Indeed, our recent experiments and DFT simulations confirmed that LaRu$_2$P$_2$, one of ThCr$_2$Si$_2$-type intermetallic compound, also exhibits the mechanical responses similar with those of CaFe$_2$As$_2$ (Supplementary Fig. 9 and Supplementary Note 5).

In summary, our results suggest the strong potential of CaFe$_2$As$_2$ as a structural material in terms of high elastic energy storage, high actuation power, low fatigue damages, and cryogenic shape memory behavior. Forming and breaking As-As type bond process of cT transition is an entirely different from a conventional martensitic-austenitic transformation process. Our results offer the possibility of developing cryogenic linear actuation technologies with a high precision and high actuation power per unit volume for deep space exploration, and more broadly, suggest a mechanistic path to a whole new class of shape memory materials, ThCr$_2$Si$_2$-structured intermetallic compounds.

Methods

**Single-crystal growth.** Single crystals of CaFe$_2$As$_2$ were grown out from a Sn flux, using conventional high-temperature solution method. Elements Ca, Fe, As, and Sn were combined together in the ratio of Ca:Fe:As:Sn = 2:3.5:4:96. Single crystals were grown by slowly cooling the Ca–Fe–As–Sn melt from 1180 °C to 600 °C at $5 \text{ °C/h}$, and then decanting o the excess liquid flux. Detailed description of the crystal growth can be found elsewhere. The obtained crystals have typical size up to $5 \times 5 \times 1 \text{ mm}^3$.

**In situ nanomechanical measurement.** Micropillars were produced using an FEI Helios Nanolab 460FIB machine. Gallium ion beam currents from 300 to 10 pA under an operating voltage of 30 kV were used from the initial to final thinning with concentric circle patterns. Note that the typical thickness of FIB damage layer is about 20 nm, which is much thinner than our pillar diameter (~2 μm). Thus, the effects of FIB damage layer on mechanical data should be negligible. Also, in our study, the size effect in superelasticity is not expected since the length scale of phase transformation is unit lattice size, which is much smaller than our pillar diameter (~2 μm). Thus, our micropillar volume should be the representative volume of the bulk. In the in situ nanomechanical test was performed at room temperature and under ultra-high vacuum condition (~$10^{-4} \text{ Pa}$) using NanoFlip (Nanomechanics, Inc., TN, USA), which is installed in a field-emission gun JEOL 6330 F scanning electron microscope (JEOL, Japan). The nominal displacement rate of 10 nm/s, which corresponds to the engineering strain rate of $0.002 \text{ s}^{-1}$, was used for all in situ compression tests in this study. The thermal drift was always smaller than 0.01 nm/μ. Thus, the typical thickness of FIB damage layer was exactly matched with the diffractometer scattering plane. Then, hydrostatic pressure was applied to a pressure cell. We were able to monitor and adjust the hydrostatic pressure by using a pressurizing intensifier. This system enabled us to control the pressure at fixed temperatures (above the He solidification line), or to scan the temperature at almost constant pressures. We determined the phase boundary between the orthorhombic and the collapsed tetragonal phases by changing pressure at a fixed temperature while monitoring the (004)$_c$ intensity and the (004)$_\text{ortho}$ reflection intensity. Also, we obtained the collapsed tetragonal ‘tetragonal’ and ‘collapsed tetragonal’-‘orthorhombic’ phase boundaries by measuring the intensity of the (004)$_c$ diffraction peak while increasing the temperature, or the intensity of the (004)$_\text{ortho}$ diffraction peaks while decreasing the temperature.

**Data availability.** All relevant data are available from the corresponding author on request.

Received: 10 December 2016 Accepted: 1 September 2017
Published online: 20 October 2017

References

1. Barrett, C. R., Tetelman, A. S. & Nix, W. D. The Principles of Engineering Materials (Prentice-Hall, 1973).
2. Hirsh, J. P. & Lothe, J. Theory of Dislocations (Krieger Publishing Company, 1982).
3. Tadaki, T., Otsuka, K. & Shimizu, K. Shape memory alloys. *Ann. Rev. Mater. Sci.* 18, 25–45 (1988).
4. Otsuka, K. & Wayman, C. M. Shape Memory Materials (Cambridge University Press, 1999).
5. Robinson, A. Metallurgy: extraordinary alloys that remember their past. *Science* 191, 934–936 (1976).
6. Omori, T. & Kainuma, R. Materials science: Alloys with long memories. *Nature* 502, 42–44 (2013).
7. San Juan, J., Nó, M. L. & Schuh, C. A. Nanoscale shape-memory alloys for ultra-high mechanical damping. *Nat. Nanotechnol.* 4, 415–419 (2009).
8. Song, Y., Chen, X., Dabade, V., Shield, T. W. & James, R. D. Enhanced reversibility and unusual microstructure of a phase-transforming material. *Nature* 502, 85–88 (2013).
9. Tanaka, Y. et al. Ferrous polycrystalline shape-memory alloy showing huge superelasticity. *Science* 327, 1488–1490 (2010).
10. Otsuka, K., Sakamoto, H. & Shimizu, K. Successive stress-induced martensitic transformations and associated transformation pseudoelasticity in Cu-Al-Ni alloys. *Acta Metall.* 27, 585–601 (1979).
11. Lai, A., Du, Z., Gan, C. L. & Schuh, C. A. Shape memory and superelastic ceramics at small scales. *Science* 327, 1505–1508 (2013).
12. Canfield, P. C. et al. Structural, magnetic and superconducting phase transitions in CaFe$_2$As$_2$ under ambient and applied pressure. *Phys. C Supercond.* 469, 404–412 (2009).
13. Ran, S. et al. Stabilization of an ambient-pressure collapsed tetragonal phase in CaFe$_2$As$_2$ and tuning of the orthorhombic-antiferromagnetic transition temperature by over 70 K via control of nanoscale precipitates. *Phys. Rev. B* 83, 144517 (2011).
14. Ran, S. et al. Control of magnetic, nonmagnetic, and superconducting states in annealed CaFe$_2$$_{(x-Cu)}$_{}$As$_2$. *Phys. Rev. B* 85, 224528 (2012).
15. Torikachvili, M. S., Bud’ko, S. L. & Canfield, P. C. Pressure induced superconductivity in CaFe$_2$As$_2$. *Phys. Rev. Lett.* 101, 057006 (2008).

**Neutron scattering measurement.** We obtained neutron scattering data by using the BT-7 spectrometer of the NIST Center for Neutron Research. The scattering data were obtained in double-axis mode with a wavelength of 2.36 Å. Higher harmonic portion of the neutron beam was eliminated by using pyrolytic graphite filters. A 10 mg single crystal was wrapped in Al-foil, and then was placed in a flat plate of the Al-alloy He-gas pressure cell. Then, a closed-cycle refrigerator was used to cool the crystal. The sample was exactly matched with the diffractometer scattering plane. Then, hydrostatic pressure was applied to a pressure cell. We were able to monitor and adjust the hydrostatic pressure by using a pressurizing intensifier. This system enabled us to control the pressure at fixed temperatures (above the He solidification line), or to scan the temperature at almost constant pressures. We determined the phase boundary between the orthorhombic and the collapsed tetragonal phases by changing pressure at a fixed temperature while monitoring the (004)$_c$ intensity and the (004)$_\text{ortho}$ reflection intensity. Also, we obtained the collapsed tetragonal ‘tetragonal’ and ‘collapsed tetragonal’-‘orthorhombic’ phase boundaries by measuring the intensity of the (004)$_c$ diffraction peak while increasing the temperature, or the intensity of the (004)$_\text{ortho}$ and (004)$_\text{ortho}$ reflection peaks while decreasing the temperature.

**DFT calculation.** The density functional theory simulations were carried out using the Vienna ab initio Simulation (VASP) package using a plane wave basis. The projector augmented wave (PAW) pseudopotentials were used in all calculations and the exchange-correlation energies were evaluated using the formulation of Perdew, Burke and Enzerhof (PBE) within the generalized gradient approximation (GGA). The energy cutoff of the plane waves was set to 450 eV and a Monkhorst Pack integration scheme of $10 \times 10 \times 5$ was used for the integration of the irreducible Brillouin zone. Most of the calculations involve the deformation of a single unit cell of CaFe$_2$As$_2$. At low temperatures, the orthorhombic structure is the stable structure with 20 atoms in its unit cell and this structure was used in all our calculations, even for non-magnetic collapsed tetragonal case. The lattice constants of the orthorhombic phase were found to be 5.60 Å, 5.49 Å and 11.48 Å and the iron moment was found to be 1.83 μ. The lattice constants agree well with experimental values while the iron moment is large, but these findings are in very good agreement with previous DFT studies.
Acknowledgements

J.T.S., K.J.D. and S.-W.L. acknowledge support from the UConn Start-up Funding, the UConn Research Excellence Program Funding, and the Early Career Faculty Grant from NASA’s Space Technology Research Grants Program. FIB work was performed using the facilities in the UConn/FEI Center for Advanced Microscopy and Materials Analysis (CAMMA). Work by P.C.C. and S.L.B. was supported by the US Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering. Their research was performed at the Ames Laboratory. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

Author contributions

J.T.S. and S.-W.L. conceived and designed the experiments and simulations, and performed in situ micro-mechanical tests. P.C.C. and S.L.B. proposed these measurements and grew a CaFe$_2$As$_2$ single crystal. P.C.C. and S.L.B. grew LaRu$_2$P$_2$ single crystal. H.P., A.M.G., and K.J. performed density functional theory calculation. H.P., A.M.G., and K.J. performed nanodentation and in situ micro-mechanical test on LaRu$_2$P$_2$. A.I.G., A.K., P.C.C. and S.L.B. performed cryogenic neutron scattering measurement under pressure. J.T.S., P.C.C., C.R.W., and S.-W.L. wrote the paper. All authors discussed the results and commented on the manuscript. Correspondence should be addressed to S.-W.L.

Additional information

Supplementary Information accompanies this paper at 10.1038/s41467-017-01275-z.

Competing interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2017