6-19-2019

Ultrahigh elastically compressible and strain-engineerable intermetallic compounds under uniaxial mechanical loading

Gyuho Song  
*University of Connecticut*

Vladislav Borisov  
*Goethe University*

William Meier  
*Iowa State University and Ames Laboratory*

Mingyu Xu  
*Iowa State University and Ames Laboratory, mxu26@iastate.edu*

Keith J. Dusoe  
*University of Connecticut*

See next page for additional authors

Follow this and additional works at: [https://lib.dr.iastate.edu/ameslab_manuscripts](https://lib.dr.iastate.edu/ameslab_manuscripts)

Part of the Condensed Matter Physics Commons, Engineering Physics Commons, and the Materials Science and Engineering Commons

Recommended Citation

Song, Gyuho; Borisov, Vladislav; Meier, William; Xu, Mingyu; Dusoe, Keith J.; Sypek, John T.; Valentí, Roser; Canfield, Paul C.; and Lee, Seok-Woo, "Ultrahigh elastically compressible and strain-engineerable intermetallic compounds under uniaxial mechanical loading" (2019). *Ames Laboratory Accepted Manuscripts*. 382.  
[https://lib.dr.iastate.edu/ameslab_manuscripts/382](https://lib.dr.iastate.edu/ameslab_manuscripts/382)

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Ultra-high elastically compressible and strain-engineerable intermetallic compounds under uniaxial mechanical loading

Abstract
Intermetallic compounds possess unique atomic arrangements that often lead to exceptional material properties, but their extreme brittleness usually causes fracture at a limited strain of less than 1% and prevents their practical use. Therefore, it is critical for them to exhibit either plasticity or some form of structural transition to absorb and release a sufficient amount of mechanical energy before failure occurs. This study reports that the ThCr2Si2-structured intermetallic compound (CaFe2As2) and a hybrid of its structure (CaKFe4As4) with 2 µm in diameter and 6 µm in height can exhibit superelasticity with strain up to 17% through a reversible, deformation-induced lattice collapse, leading to a modulus of resilience orders of magnitude higher than that of most engineering materials. Such superelasticity also can enable strain engineering, which refers to the modification of material properties through elastic strain. Density functional theory calculations and cryogenic nanomechanical tests predict that superconductivity in CaKFe4As4 could be turned on/off through the superelasticity process, before fracture occurs, even under uniaxial compression, which is the favorable switching loading mode in most engineering applications. Our results suggest that other members with the same crystal structure (more than 2500 intermetallic compounds) and substitution series based on them should be examined for the possibility of manifesting similar superelastic and strain-engineerable functional properties.

Disciplines
Condensed Matter Physics | Engineering Physics | Materials Science and Engineering

Authors
Gyuho Song, Vladislav Borisov, William Meier, Mingyu Xu, Keith J. Dusoe, John T. Sypek, Roser Valenti, Paul C. Canfield, and Seok-Woo Lee

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/ameslab_manuscripts/382
Ultrahigh elastically compressible and strain-engineerable intermetallic compounds under uniaxial mechanical loading

Cite as: APL Mater. 7, 061104 (2019); https://doi.org/10.1063/1.5087279
Submitted: 31 December 2018 . Accepted: 13 May 2019 . Published Online: 19 June 2019

Gyuho Song, Vladislav Borisov, William R. Meier, Mingyu Xu, Keith J. Dusoe, John T. Sypek, Roser Valentí, Paul C. Canfield, and Seok-Woo Lee

ARTICLES YOU MAY BE INTERESTED IN

Large-area MoS2-MoOx heterojunction thin-film photodetectors with wide spectral range and enhanced photoresponse
APL Materials 7, 061101 (2019); https://doi.org/10.1063/1.5094586

Determining interface structures in vertically aligned nanocomposite films
APL Materials 7, 061105 (2019); https://doi.org/10.1063/1.5099204

Defects at the surface of β-Ga2O3 produced by Ar plasma exposure
APL Materials 7, 061102 (2019); https://doi.org/10.1063/1.5109025
Ultrahigh elastically compressible and strain-engineerable intermetallic compounds under uniaxial mechanical loading

Cite as: APL Mater. 7, 061104 (2019); doi: 10.1063/1.5087279
Submitted: 31 December 2018 • Accepted: 13 May 2019 • Published Online: 19 June 2019

Gyuho Song, Vladislav Borisov, William R. Meier, Mingyu Xu, Keith J. Dusoe, John T. Sypek, Roser Valentí, Paul C. Canfield, and Seok-Woo Lee

AFFILIATIONS
1Department of Materials Science and Engineering and Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Unit 3136, Storrs, Connecticut 06269-3136, USA
2Institute of Theoretical Physics, Goethe University, Frankfurt am Main, D-60438 Frankfurt am Main, Germany
3Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

Electronic mail: seok-woo.lee@uconn.edu

ABSTRACT
Intermetallic compounds possess unique atomic arrangements that often lead to exceptional material properties, but their extreme brittleness usually causes fracture at a limited strain of less than 1% and prevents their practical use. Therefore, it is critical for them to exhibit either plasticity or some form of structural transition to absorb and release a sufficient amount of mechanical energy before failure occurs. This study reports that the ThCr$_2$Si$_2$-structured intermetallic compound (CaFe$_2$As$_2$) and a hybrid of its structure (CaKFe$_4$As$_4$) with 2 µm in diameter and 6 µm in height can exhibit superelasticity with strain up to 17% through a reversible, deformation-induced lattice collapse, leading to a modulus of resilience orders of magnitude higher than that of most engineering materials. Such superelasticity also can enable strain engineering, which refers to the modification of material properties through elastic strain. Density functional theory calculations and cryogenic nanomechanical tests predict that superconductivity in CaKFe$_4$As$_4$ could be turned on/off through the superelasticity process, before fracture occurs, even under uniaxial compression, which is the favorable switching loading mode in most engineering applications. Our results suggest that other members with the same crystal structure (more than 2500 intermetallic compounds) and substitution series based on them should be examined for the possibility of manifesting similar superelastic and strain-engineerable functional properties.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5087279
One of the most known examples would be the increase in carrier mobility in elastically strained silicon under biaxial strain. Because the size effect on elastic strain has been widely observed in brittle materials at small length scales, it could also be seen in novel intermetallic compounds at the nano-/micrometer scale.

Recently, high temperature Fe-based superconductors have drawn strong attention due to their superconducting capability even in the presence of magnetic Fe, which has been regarded as a harmful element for superconductivity.\(^{23,32}\) Now, they are regarded as a great material system that allows the study of relationship between superconductivity and magnetism. ThCr\(_2\)Si\(_2\)-structured Fe-based pnictides have been extensively studied due to their strong pressure sensitivity of structure and electronic/magnetic properties.\(^{23}\) Particularly, CaFe\(_2\)As\(_2\) single crystals undergo collapsed tetragonal (cT) phase transition, which leads to \(-10\%\) reduction of the c-axis lattice parameter under hydrostatic pressure. We also performed uniaxial mechanical tests on CaFe\(_2\)As\(_2\) micropillars and observed unique mechanical behaviors including \(-13\%\) of superelasticity, lastic fatigue resistance, cryogenic shape memory effects, and micaceous plasticity.\(^{32,34}\) Notably, magnetism of CaFe\(_2\)As\(_2\) changes from paramagnetic (or antiferromagnetic) to nonmagnetic states when the cT transition occurs.\(^{23}\) Thus, strain engineering of magnetism is possible for CaFe\(_2\)As\(_2\) or its related structures.

Recently, the hybrid structures of Fe-based pnictides, CaKFe\(_2\)As\(_4\), have been actively investigated due to its high temperature superconductivity (\(T_c \sim 35\,K\)).\(^{35}\) The previous study confirmed that superconductivity can be switched off under hydrostatic pressure through the half collapsed tetragonal (hcT) transition around the Ca atom.\(^{29}\) However, uniaxial mechanical tests on CaKFe\(_2\)As\(_4\) have never been done, and it should be interesting to see how differently CaKFe\(_2\)As\(_4\) behaves, compared to CaFe\(_2\)As\(_2\) in terms of superelasticity. The insertion of large K atoms into the lattice makes the As–As distance around the K atom larger. The larger interplanar spacing could allow the larger linear elastic strain simply because the widely spaced layers could be compressed more. However, the large As–As distance would make the As–As bond formation more difficult. Thus, the competition of these two factors could affect the total elastic strain. In addition, we noticed that the plastic slip (or shear fracture) of CaFe\(_2\)As\(_4\) occurs in the 1/3[3 1 1]/1 (0 3 0) slip system under compression along the c-axis. Due to the larger c-axis length of CaKFe\(_2\)As\(_4\),\(^{36}\) the slip vector of CaKFe\(_2\)As\(_4\) in the same slip system should be larger than that of CaFe\(_2\)As\(_2\), implying that CaKFe\(_2\)As\(_4\) would exhibit a higher yield strength, based on the Peierls-Nabarro model.\(^{30,31}\) In this sense, CaKFe\(_2\)As\(_4\) could exhibit the elastic strain larger than that of CaFe\(_2\)As\(_2\).

In this study, therefore, we performed uniaxial micropillar compression tests and Density Functional Theory (DFT) calculation to investigate the superelastic properties of CaKFe\(_2\)As\(_4\) and compared the mechanical data with those of CaFe\(_2\)As\(_2\). We found a giant elastic limit, up to 17\%, in CaKFe\(_2\)As\(_4\), under uniaxial compression along the c-axis of their unit cells. Density functional theory calculations revealed that this enormously large elastic strain primarily results from atomic bond formation around the Ca atom and local elastic compliance around the K atom. Also, the cyclic compression test on CaKFe\(_2\)As\(_4\) showed that the superelastic deformation over 10\% strain is completely reversible when the applied force is relaxed. This uniaxial process is entirely distinct from the conventional shear-based superelastic mechanism, martensite-austenite phase transformation of shape memory alloys and ceramics.\(^{37-39}\) Moreover, we also used our custom-built \textit{in situ} cryogenic micromechanical testing system to investigate the effects of temperature on the first hcT transition, which is known to remove superconductivity in CaKFe\(_2\)As\(_4\). We found that the onset stress of the first hcT transition near the superconducting transition temperature is much lower than the fracture strength. This result suggests that there is a strong possibility to see the superconductivity switching even under uniaxial compression before fracture occurs.

CaFe\(_2\)As\(_2\) is grown from a Sn-rich solution, and CaKFe\(_2\)As\(_4\) was grown from excess FeAs. The constituent materials were put in alumina crucibles, which are located in an amorphous silica ampule. Single crystals were slowly grown under slow cooling in a furnace and were quickly decanted using a centrifuge. The detailed descriptions of the solution growth of our crystals are also available elsewhere.\(^{32,35}\) Micropillars are fabricated using focused-ion beam (FIB) milling, Helios Nanolab 460F1 (Thermo Fisher, USA). 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. Because the typical thickness of the FIB damage layer is about 20 nm, which is much thinner than our pillar diameter (\(\sim 2\,\mu m\)), we expect negligible effects of FIB damage on the mechanical data. \textit{In situ} nanomechanical test was performed at room temperature and under an ultrahigh vacuum condition (\(<10^{-4}\) Pa) using the NanoFlip\(^{34}\) (KTL-Tencor, USA), which is installed in a field-emission gun JEOL 6335F scanning electron microscope (JEOL, Japan). A nominal displacement rate of 10 nm/s, which corresponds to the engineering strain rate of \(-0.002\,s^{-1}\), was used for all \textit{in situ} compression tests in this study. Stress calculations for experiments were done with the Sneddon punch correction using the effective Young’s modulus that can be measured by nanoindentation.\(^{34}\) The recorded video was often used to visually confirm that our strain measurements were accurate. A liquid nitrogen and helium cryostat (ST-100) was used to perform nanomechanical testing at low temperatures to investigate the temperature effects on mechanical properties. The temperature of the diamond tip was maintained to be similar to that of the sample by using thermal equilibration, leading to a thermal drift below 0.5 nm/sec at all times. A detailed description of our cryogenic system is also available in the supplementary material (Figs. S1 and S2, and Supplementary Note 1). Contact stiffness was measured during compression testing by applying a force oscillation with \(10\,nN\) in amplitude and 200 Hz in frequency and measuring the resultant displacement oscillation. Contact stiffness data often show the clearer evidence of lattice collapse than the stress-strain curve.\(^{37}\) The contact stiffness, \(S\), is measured by

\[ S = \left[ \frac{P_{OS}}{\pi c \phi} \cos \phi - \left( K_S + m_\phi^2 \right) K_f \right] ^{-1}, \tag{1} \]

where \(P_{OS}\) is the magnitude of force oscillation, \(h(\omega)\) is the magnitude of resulting displacement oscillation, \(\omega\) is the frequency of oscillation, and \(\phi\) is the phase angle between the force and displacement signals. \(K_S\) and \(K_f\) are the stiffness of the leaf spring and indenter frame, respectively.\(^{34}\) When structural collapse occurs, the phase angle becomes smaller, providing a lower contact stiffness.
This method is useful to capture the availability of structural collapse during a micromechanical test.

In our density functional theory calculations, structure optimization in the CaKFe$_4$As$_4$ system was performed using the state-of-the-art projector-augmented wave method" and the generalized-gradient approximation available in the Vienna Ab initio Simulation Package (VASP) code. The energy cutoff was set to 800 eV, and the k-mesh dimensions were $5 \times 5 \times 5$. Although the system does not show a long-range magnetic order, the inclusion of Fe local moments in the simulation is necessary for a correct description of structural transitions under pressure, as detailed in previous studies. For that reason, we imposed the "frozen" spin-vortex spin configuration on the Fe sublattice which approximates the effect of spin fluctuations present in this material. In this work, we simulate the uniaxial [001]-strain conditions by varying the c-lattice parameter and calculating the total energies of CaKFe$_4$As$_4$ structures optimized for different a-lattice parameters.

The energy position of the As 4p orbitals across the Ca sublattice which approximates the effect of spin fluctuations present in this material. In this work, we simulate the uniaxial [001]-strain conditions by varying the c-lattice parameter and calculating the total energies of CaKFe$_4$As$_4$ structures optimized for different a-lattice parameters.

allowed to estimate the equilibrium lattice parameters for a given value of strain. In the final step, the internal atomic positions are optimized for the fixed lattice dimensions and the stress value along the c-axis was obtained. The electronic properties of the optimized structures were calculated using the all-electron full-potential localized orbitals (FPLO) basis set code within the GGA approach. The half-collapsed tetragonal transition was captured by inspecting the energy position of the As 4p antibonding orbitals near the Ca layer. In order to illustrate the half-collapse transitions in CaKFe$_4$As$_4$ under the uniaxial load, we plot the real-space distribution of the electron density associated with the As 4p orbitals near the Ca sublattice which approximates the effect of spin fluctuations present in this material.

Bulk single crystals [Figs. 1(a) and 1(b)] of ThCr$_2$Si$_2$-type intermetallic compound (CaFe$_2$As$_2$) and its hybrid structure (CaKFe$_4$As$_4$) were grown using a solution growth method, and cylindrical micropillars with ~2 µm in diameter and ~6 µm in height were fabricated along the [0 0 1] direction using focused-ion beam (FIB) milling. Note that the CaKFe$_4$As$_4$ structure can be thought of as a periodic replacement of half of the Ca in CaFe$_2$As$_2$ with K in an alternating order along the c-axis, and it looks like a hybrid of CaFe$_2$As$_2$ and KFe$_2$As$_2$. The representative stress-strain data of CaFe$_2$As$_2$ and CaKFe$_4$As$_4$ show a large compressive elastic limit of 10.5% and 17%, respectively [Figs. 1(c) and 1(d)].
For comparison, the superelastic regime of the stress-strain data for superelastic zirconia\textsuperscript{44} and NiTi\textsuperscript{45} micropillars, both of which are well-known superelastic materials, are plotted together with our CaKFe\textsubscript{4}As\textsubscript{4} data [Fig. 1(d)]. It is clearly seen that our materials exhibit much greater performance in terms of both yield strength and elastic limit. We identify three stages in the stress-strain data. Interestingly, the nonlinear stress-strain responses of our crystals resemble those of typical superelastic shape memory alloys, suggesting that the uniaxial deformation of our crystals would induce a structural transition, too. Also, the deformation is completely reversible when the applied load is relaxed (Fig. S3 of the supplementary material and the inset of Fig. S5) and is repeatable under cyclic deformation (Ref. 28 and Fig. S4 of the supplementary material). Note that we have never seen any evidence of shear deformation from more than 20 samples tested. The real-time SEM videos always showed a clean surface until fracture occurs. Thus, our superelasticity does not appear to be related to any conventional shear-based mechanism such as martensite-austenite phase transformation, which forms shear bands and causes a significant lateral displacement particularly in the case of a single crystal.\textsuperscript{46}

The decrease in contact stiffness within stage II looks counter-intuitive [Figs. 1(e) and 1(f)] because the contact stiffness of a solid material usually increases during compression.\textsuperscript{10} Hoffmann and Zheng hypothesized that such a decrease would be possible through a process of forming and breaking Si–Si-type bonds in ThCr\textsubscript{2}Si\textsubscript{2}-type structures under uniaxial compression along the c-axis.\textsuperscript{27,47–49} Thus, the decrease in contact stiffness indeed results from a strain-induced structural collapse through As–As bond formation in these structures. On the course of deformation, the formation of As–As bonds makes materials more elastically compliant, but once the lattice collapse is almost complete, the contact stiffness increases again. Thus, stages I and III would correspond to the elastic deformation before and after formation of As–As bonds, respectively. Stage II would correspond to the deformation on the course of As–As bond formation.

Note that the elastic limit 15%–17% of CaKFe\textsubscript{4}As\textsubscript{4} is truly extraordinary, compared to any other shape memory intermetallic compounds, as well as CaFe\textsubscript{2}As\textsubscript{2} (11%–14%) in this study [Figs. 1(d) and 2(a)]. Our Density Functional Theory (DFT) calculations of CaKFe\textsubscript{4}As\textsubscript{4} under uniaxial strain find two half-collapsed tetragonal (hcT) transitions for this system [Figs. 2(b), 2(c), and 2(d)], while the full-collapsed tetragonal (cT) transition is observed in CaFe\textsubscript{2}As\textsubscript{2}.\textsuperscript{27,48} This result is qualitatively similar to the results of application of hydrostatic pressure.\textsuperscript{29,49} Non-spin-polarized electron density associated with the As-4p\textsubscript{z} orbitals clearly shows the presence of two separate hcT transitions in CaKFe\textsubscript{4}As\textsubscript{4} at different strains [Figs. 2(c) and 2(d)]. In CaKFe\textsubscript{4}As\textsubscript{4}, the first hcT appears at a strain of \(\sim0.05–0.08\) when As atoms around Ca form As–As bonds. The smaller atomic radius (231 pm) of the Ca atom allows a shorter As–As distance (3.107 Å) around it, leading to the formation of As–As bonds under a low compressive strain (\(\sim0.05\)). Thus, the structural transition in stage II of CaKFe\textsubscript{4}As\textsubscript{4} [Fig. 1(d)] would be related to the deformation after the onset of the first hcT transition. Based on our DFT data, the second hcT occurs at strain values near the

![FIG. 2. Superelasticity of CaKFe\textsubscript{4}As\textsubscript{4}. (a) Snapshots of in situ video right before contact with the diamond tip and right before failure (scale bar, 1 \(\mu\text{m}\)). (b) DFT simulation results of engineering stress-strain data. Red box represents the experimental data range that is limited by fracture. Note that the sharp drop of engineering stress around 0.1 strain occurs due to the collapse of magnetic moments, which are intentionally introduced to mimic the paramagnetic state. Due to random distribution of magnetic moments at a finite temperature in a real system, this effect would spread within stage II. Stage IV corresponds to the elastic deformation after the second hcT transition, which cannot be seen in a real system due to fracture in stage III. Non-spin-polarized electron density in the ac plane associated with the As-4p\textsubscript{z} orbitals near (c) Ca and (d) K at different strains. (c) shows clear bond formation across the Ca-layer by 0.05 strain, and (d) shows clear bond formation across the K-layer by 0.18 strain.](https://scitation.aip.org/content/aip/journal/apm/7/661104-4)
experimentally measured elastic limit (fracture strain), ~0.18–0.19. At this transition, As atoms around K form As–As bonds. Since the larger atomic radius of K (280 pm) leads to a longer-distance between the As–As layer (4.205 Å), a larger elastic strain is needed to reach the second hcT transition. Thus, stage III of CaKFe₄As₄ would correspond to the gradual formation of As–As bonds around the K atom. All these results also explain a higher rate of structural collapse per strain for the full collapse in CaFe₂As₂ (~15 GPa) than that for the half collapse in CaKFe₄As₄ (~31 GPa) for stage II deformation [Figs. 1(c) and 1(d)].

We also carefully monitored our DFT data to examine the contribution of As–As layers near a K atom to the total elastic strain. The interlayer distance of As–As layer around a K atom is 3.2816 Å near the elastic limit. By considering that it is 4.205 Å before compression, its change contributes to (4.205 Å–3.2816 Å)/(12.6205 Å, initial c-length) ≈0.073 of strain (~41% of the total elastic limit), which is remarkably high [the third figure in Fig. 2(d) and Fig. S5 of the supplementary material]. This result implies that the larger atom size of K makes the formation of As–As bond more difficult but makes the region between As–As layers around the K atom more elastically compliant. Also, note that our elastic limit (~17%) is close to the elastic strain at which the second hcT occurs in our DFT data. The driving force of the second hcT, i.e., the formation of As–As bonds around the K atom, would partially contribute to a large elastic compliance. In view of these observations, we attribute the extraordinary elastic limit of CaKFe₄As₄ to the presence of these two hcT transitions and the larger atomic size of K. Therefore, it is important to control bond formation and local elastic compliance to tune the superelastic properties.

The elastic limits of our intermetallic compounds are exceptionally high, compared to other superelastic materials even in similar length scales [Fig. 3(a); Fig. S6 and Supplementary Note 2 of the supplementary material]. The comparable superelastic strain can be observed only when the dimension of shape memory intermetallic compounds becomes close to 100 nm. Usually, materials become stronger when the sample dimension is reduced to the nanometer length scale for various reasons. For instance, NiTi nanopillars with 150 nm in diameter exhibit an improved yield strength, leading to a 15% elastic limit. If the micrometer length-scale of our specimen is considered, the observed elastic limit (~10%–17%) is absolutely outstanding. Note that we also observed size effect in CaFe₂As₂. Its submicron sized pillars exhibit ~17% elastic strain (Fig. S7 of the supplementary material). This size effect could be related to the weakest-link mechanism. Brittle materials often exhibit higher strength and higher elastic limit when they become extremely small. This has been observed in various brittle materials, such as ceramic, diamond, metallic glass, and nanowires, and the weakest-link mechanism is one of the most widely accepted ideas. If a sample dimension becomes larger, it is more likely to have weaker defects that can induce brittle failure at a lower strength. Vice versa, fracture strength (also, elastic limit) increases as the sample dimension becomes smaller because it is unlikely to find the weak defect. If the diameter of our specimens is also reduced further down to sub-100 nm, it would be possible for them to show much greater performance, and the detailed analysis on the size effect will be presented in a separate work.

It is also worthwhile to compare the elastic performance with other advanced engineering materials. The Ashby chart has been extensively used when material properties of new materials need to be compared with those of other materials. Our materials are located in the E–σₙ space of the Ashby chart [Fig. 3(b)], where σₙ is the yield strength and E is Young’s modulus. Due to the non-linearity of the stress-strain curve, the effective Young’s modulus (Eₑffective) can be estimated by Eₑffective = E₂/σₙ, where R is the modulus of resilience. The modulus of resilience is the maximum mechanical
energy absorption per unit volume prior to yielding and can be calculated by integrating the stress-strain curve from 0 to the elastic limit. In the $E-\sigma_c$ space of the Ashby chart, as a material is located closer to the right-bottom corner, it can absorb higher mechanical energy per unit volume. Note that both CaFe$_2$As$_2$ and CaKFe$_4$As$_4$ are located in the white space, indicating their superior elastic performance to absorb large amounts of strain energy before yielding [Fig. 3(b)]. The average moduli of resilience are 143 MJ/m$^3$ and 291 MJ/m$^3$ for CaFe$_2$As$_2$ and CaKFe$_4$As$_4$, respectively (Figs. S8 and S9 of the supplementary material). By considering the accurate measurement of the stress-strain curve and their reproducibility, our $R$ data are accurate for our micropillar samples. Note that the total strain energy absorption of our specimen is orders of magnitude higher than most engineering materials at both bulk and micrometer scales such as elastomers (~1 MJ/m$^3$), advanced composites (~0.5 MJ/m$^3$), conventional shape memory alloys (~50 MJ/m$^3$), metallic nanopillars (~10 MJ/m$^3$), and superelastic ceramic micropillars (~50 MJ/m$^3$). Semiconductor or ceramic nanowires sometimes show the extremely high modulus of resilience (>10000 MJ/m$^3$) due to their defectfree structure in their ultrathin diameter (~50 nm) [Fig. 3(b) and Supplementary Note 3 of the supplementary material]. In sum, Figs. 3(a) and 3(b) show the giant superelasticity of CaKFe$_4$As$_4$ as well as the great potential of Fe-based pnictide superconductors as a superelastic material.

The giant elastic limit of our materials could make strain-engineering possible. Strain-engineering refers to a significant modification of the properties of solid materials by applying an elastic strain.\textsuperscript{15} Similar material to our material, Co-doped CaFe$_2$As$_2$, CaFe$_{1-x}$Co$_x$As$_2$, shows the superconductivity switching by the application of biaxial deformation on the $ab$ plane, which changes the $c/a$ ratio of the unit cell and results in the significant shift of the superconductivity region in the temperature-composition phase diagram.\textsuperscript{58,59} This strong effect of the $c/a$ ratio on superconductivity could extend to our CaKFe$_4$As$_4$ system, which is also a high temperature superconductor ($T_c \approx 35$ K), under c-axis uniaxial compression that should change the $c/a$ ratio much more significantly.

A previous experimental study with hydrostatic pressure demonstrated that the superconductivity of CaKFe$_4$As$_4$ can be turned off reversibly by the application of hydrostatic pressure of 4 GPa when the system undergoes the first hcT transition.\textsuperscript{7} That is, the formation of As–As bonds around the Ca atoms is a key process to turn off superconductivity. We recently developed an in situ cryogenic micromechanical testing system (Figs. S1 and S2, and Supplementary Note 1 of the supplementary material) and confirmed that the first hcT transition occurs only around 1 GPa under uniaxial compression without failure [Fig. 4(a)]. Interestingly, the structural collapse behavior in CaKFe$_4$As$_4$ is insensitive to a change in the temperature, whereas pure and Co-doped CaFe$_2$As$_2$ exhibits strong temperature sensitivity (Fig. S10 of the supplementary material). These different temperature dependences under uniaxial stress are consistent with the hydrostatic pressure experimental data.\textsuperscript{29,49}

The weak temperature dependence of CaKFe$_4$As$_4$ is not fully understood, yet. However, there are several indirect experimental and computational evidence to explain the different temperature sensitivity between CaKFe$_4$As$_4$ and CaFe$_2$As$_2$. Several computational studies suggested that the distance between atomic layers in Fe-based pnictides is strongly affected by the distribution of magnetic moments.\textsuperscript{60} Interestingly, the magnetic susceptibility of CaKFe$_4$As$_4$ exhibits a weak temperature dependence.\textsuperscript{41} This result implies that the magnetic structure or the spin ordering does not change with the temperature so that the c-axis does not change much with the temperature.\textsuperscript{61} As a consequence, mechanical properties are

![FIG. 4. Cryogenic nanomechanical test and DFT simulation near the onset of the first hcT transition. (a) Engineering stress-strain curves of CaKFe$_4$As$_4$ at various cryogenic conditions. The arrow indicates the onset of the first hcT transition. Orbital-resolved non-spin-polarized band structure of CaKFe$_4$As$_4$ under (b) uniaxial and (c) hydrostatic pressure before and after the first hcT (hcT) transition. 4$p_z$ orbitals near the Ca (K) layer are marked by blue (orange) color. Upon the hcT transition, the antibonding As orbitals shift above the Fermi level. These results show that the change in electronic structure under uniaxial compressive stress (strain) does not differ from that under hydrostatic pressure, implying that the change in electronic properties (here, superconductivity) will be similar under both uniaxial compressive stress and hydrostatic pressure.](image-url)
insensitive to temperature, too. This scenario is consistent with our experimental data in Fig. 4(a).

CaFe$_2$As$_2$ behaves differently. Magnetic susceptibility decreases with temperature when it is the paramagnetic tetragonal structure. Inelastic neutron scattering measurement showed that as the temperature decreases, the short-range antiferromagnetic ordering increases. At the same time, the c-axis length decreases substantially with the temperature. Thus, magnetism and structure of CaFe$_2$As$_2$ are more sensitive to temperature than CaKFe$_2$As$_4$. Interestingly, once CaFe$_2$As$_2$ becomes antiferromagnetic orthorhombic structure at a temperature below the transition temperature, it becomes magnetically rigid because magnetic ordering does not occur anymore. Then, the c-axis length of CaFe$_2$As$_2$ does not change much with the temperature, as that of CaKFe$_2$As$_4$ does. This is probably why the onset stress of cT transition drastically decreases when CaFe$_2$As$_2$ is tetragonal but becomes nearly constant once CaFe$_2$As$_2$ becomes antiferromagnetic orthorhombic structure under hydrostatic pressure and uniaxial stress (Fig. S10c of the supplementary material shows the weak temperature dependence between 40 K and 100 K).

Our DFT simulation confirms that the formation of As–As bonds and the change in electronic structure under uniaxial compression are similar to those under hydrostatic compression [Figs. 4(b) and 4(c)]. A similar situation has been found in CaFe$_2$As$_2$ when comparing the electronic structure under uniaxial and hydrostatic stress. These results make sense because the deformation along the c-axis is much more significant than that along the a- and b-axis direction even under hydrostatic pressure due to the large elastic compliance and As–As bond formation along the c-axis. Under the assumption that the origin of superconductivity is linked to the electronic and magnetic properties of the system, these results suggest that superconductivity could also be switched off by inducing the first hcT transition (the formation of As–As bond around a Ca atom) under uniaxial compression. Therefore, our experimental and computational results strongly suggest that the superconductivity of CaKFe$_2$As$_4$ could be reliably turned on and off at the onset of the first hcT transition (~1 GPa) without any fracture or plastic deformation, even under uniaxial compression. By considering the presence of the onset and offset of the first hcT transition in stage II, CaKFe$_2$As$_4$ would begin to show the finite resistivity at the uniaxial stress above ~1 GPa and would become completely nonsuperconducting above ~2.7 GPa (Fig. 5). Note that our result does not provide the direct evidence of superconductivity switching, yet. Resistivity measurement or permanent magnetic field measurement would be necessary under uniaxial compression to prove our prediction. By considering all experimental and computational data, superconductivity switching is likely to occur even under uniaxial deformation. Thus, electrical and magnetic measurements at small length scales are considered as the next step we would like to pursue.

Strain-engineering is usually possible when a material can absorb a large amount of strain without permanent deformation. Hydrostatic stress or biaxial stress would often be regarded as a convenient way to see the strain effect because the maximum shear stress is zero or too low to cause plastic deformation or fracture. Thus, it is rarely rare to see a substantial strain effect on material properties in brittle intermetallic compounds, particularly under a uniaxial strain condition, because the shear stress is usually sufficiently high to cause brittle failure too easily. In contrast, the structural transition in our intermetallic compounds, CaFe$_2$As$_2$ and CaKFe$_2$As$_4$, through the formation of covalent bonds leads to a giant uniaxial elastic strain, which can cause substantial changes in their electronic and magnetic properties before failure, even under uniaxial mechanical loading. The uniaxially loaded superconductivity switching capability may never be imagined in conventional oxide-base superconductors, which have no superelasticity mechanism and easily shatter at a small elastic limit under uniaxial stress due to their extreme brittleness. In addition, our previous experimental studies also demonstrated that CaFe$_2$As$_2$ could exhibit shape memory effect and thermal actuation under cryogenic environments and have a strong potential for cryogenic actuation technology for space exploration. Some groups of CaKFe$_2$As$_4$ structured intermetallic compounds are regarded as quantum materials that exhibit unique electronic and magnetic properties. More interestingly, ThCr$_2$Si$_2$-type and its related structures have been considered to be one of the most populous of all crystal structure types. There are nearly 2500 ThCr$_2$Si$_2$-structured intermetallic compounds. Even non-FeAs-based compounds demonstrate the same superelasticity mechanism. If we consider their hybrid structure, such as CaKFe$_2$As$_4$, there could be some groups of similar superelastic intermetallic compounds. Also, their microstructure and composition can easily be tuned through heat treatment and solid solutionization. Thus, our observation can be extended to search for a large group of superelastic and strain-engineerable functional materials. Computer simulations with machine-learning could be extremely beneficial to rapidly
identify compounds with these desired properties.\textsuperscript{66,67} In sum, our discovery of superelasticity and strain-engineerability under “uni-axial” mechanical loading will lead to a grand research opportunity in materials science, solid-state physics, device engineering, and computer simulations.

See supplementary material for the additional mechanical data, the description of in situ cryogenic nanomechanical testing system, and in situ videos.

G. Song, K.J. Dusoe, J.T. Sypek, and S.-W Lee acknowledge support from UConn Research Excellence Program Funded, the Early Career Faculty Grant from NASA’s Space Technology Research Grants Program, and GE Fellowship. FIB work was performed using the facilities in the Uconn/Thermo Fischer Scientific Center for Advanced Microscopy and Materials Analysis (CAMMA). Work by P.C. Canfield, W.M. Meier, and M. Xu was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering. Their research was performed at the Ames Laboratory. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. W.M. Meier was also funded by the Gordon and Betty Moore Foundation’s EPIQS Initiative through Grant No. GBMF4411. Work by R. Valentí and V. Borisov was supported by DFG Sonderforschungsbereich TRR 49, and the center for supercomputing (CSC) in Frankfurt. V. Borisov was also partially supported by Gordon and Betty Moore Foundation’s EPIQS Initiative through Grant No. GBMF4411.

REFERENCES


