



## Modeling pseudo-elastic behavior in small-scale ThCr<sub>2</sub>Si<sub>2</sub>-type crystals

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### ABSTRACT

Crystals of the ThCr<sub>2</sub>Si<sub>2</sub>-type structure comprise a large class of known compounds, and observations of superconductivity in some of the compounds generated significant interest in these materials. Recently, nano-indentation experiments have shown that at room temperature, small-scale crystals of CaFe<sub>2</sub>As<sub>2</sub> exhibit pseudo-elastic behavior with recoverable strains of over 10%. These experiments also demonstrate the potential for shape memory effects at cryogenic temperatures, behavior which has previously been related to its magnetic phase transitions. In this work, the phase transitions of CaFe<sub>2</sub>As<sub>2</sub> are investigated using density functional theory (DFT) in conjunction with analytical models. The models demonstrate that both uniaxial and hydrostatic loading can give rise to pseudo-elastic behavior. These models are then applied to LaRu<sub>2</sub>P<sub>2</sub>, which does not exhibit a magnetic phase change, but is still found to have a similar pseudo-elastic response. A suite of parameters useful in quantifying the complex responses of these compounds is presented and it is demonstrated that *c*-axis strain is the critical loading parameter in predicting the pseudo-elastic behavior. These results provide a method of connecting local chemical tuning to macroscopic behavior.

### 1. Introduction

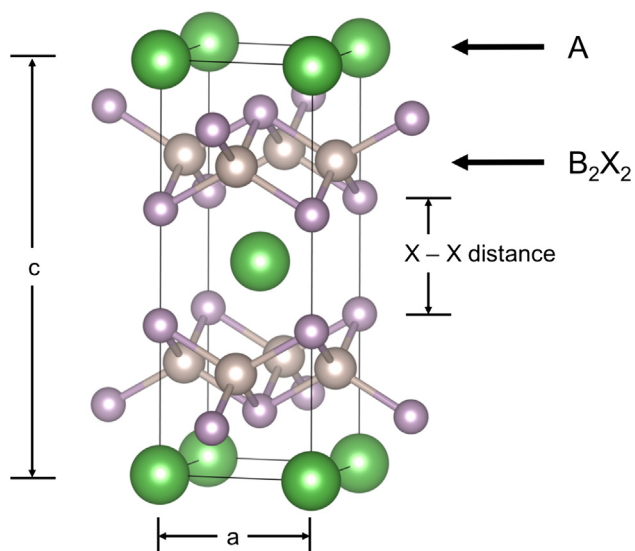
The 1:2:2 intermetallic compounds which have the ThCr<sub>2</sub>Si<sub>2</sub> crystal structure are a widely studied class of materials. These compounds were first identified in 1963 [1] and more than 400 of these compounds have since been identified [2]. Interest was furthered by the discovery of superconductivity within this class of materials with the initial discovery occurring in the lanthanum-based compounds [3]. Two subclasses of these compounds, the iron-pnictides and the iron-chalcogenides, are of particular importance because they have notably high superconducting critical temperatures (as high as 30 K) [4]. A related family of compounds, the 1:1:1:1 iron-pnictides have been reported to exhibit superconductivity above 40 K [5]. This has garnered significant interest since these materials form a class of superconductors with over 30 known examples [6,7]. It was later discovered that it is possible to enhance the superconductivity in these compounds through the application of hydrostatic pressure [8], including increasing the superconducting temperature of LaRu<sub>2</sub>P<sub>2</sub> from 3.8 K to 5.8 K under hydrostatic compression [9]. LaRu<sub>2</sub>P<sub>2</sub> had the highest superconducting temperature of the 1:2:2 compounds before the discovery of the iron-

pnictides [10,11]. However, it was found that above a certain pressures, the superconductivity disappears entirely [12].

Further investigations of this behavior [13] uncovered phase transitions which were suggested by Hoffmann and Zheng [2], who highlighted the importance of the P–P bond length between [Mn<sub>2</sub>P<sub>2</sub>] layers in AMn<sub>2</sub>P<sub>2</sub> compounds. They pointed out that some compounds exist in crystal structures with P–P distances greater than the standard P–P covalent bond length, while others have distances which are shorter. Fig. 1 shows the ThCr<sub>2</sub>Si<sub>2</sub> crystal structure, illustrating the layered nature of this crystal, which is typically comprised of a low-valency metal (such as an alkali metal, alkaline earth metal, or a rare earth metal), a transition metal, and a nonmetal or metalloid. The structure can alternatively be thought of as alternating layers of A<sup>2+</sup> and [B<sub>2</sub>X<sub>2</sub>]<sup>2-</sup> ions [2]. Note that the layered structure creates an X–X bond length that can be equal to or exceed the covalent bond length. This suggests that it is possible in some of these compounds to create covalent bonds between the phosphorous atoms by compressing the crystal structure along its *c*-axis. If the competition between the Coulombic interactions and covalent bonding is such that a local minimum exists at the covalent bond length, then a phase transition is possible

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**Fig. 1.** The  $\text{ThCr}_2\text{Si}_2$  crystal structure has a tetragonal unit cell with alternating layers of A and B-X. The original identified structure has a tetragonal unit cell, whose c-axis is at least twice as long as the side-length [1].

resulting in a collapsed version of the  $\text{ThCr}_2\text{Si}_2$  crystal structure.

In the iron-based  $\text{ThCr}_2\text{Si}_2$  compounds, antiferromagnetic ordering of the magnetic moments on the iron atoms is commonly observed at low temperatures [8]. The ordering of the magnetic moments causes the diagonals of the base of the tetragonal cell (Fig. 1) to expand unequally. The resulting lattice distortion changes the crystal structure from body-centered tetragonal to a face-centered orthorhombic (Fig. 2(b)). Above the Néel temperature, the magnetic moments randomize, eliminating the structural differences between the  $a$  and  $b$  axes of the orthorhombic crystal, resulting in a phase change from low temperature orthorhombic back to the tetragonal crystal structure [14]. Arguably, the most well-studied compound is  $\text{CaFe}_2\text{As}_2$  [8,15,16]. In this compound, three different phases have been identified as a function of temperature and pressure, as shown in Fig. 2(a). At low temperatures and pressures, antiferromagnetic ordering dominates and the crystal structure is orthorhombic. Above the Néel temperature, which is roughly 170 K for  $\text{CaFe}_2\text{As}_2$  [13,17,18], the material becomes paramagnetic and the crystal structure transforms to tetragonal. However, at high pressures, the crystal structure collapses along the  $c$ -axis and the tetragonal unit cell becomes significantly shorter [19] and the crystal becomes non-magnetic. Similar magnetic ternary compounds also exhibit magnetic phase transitions such as  $\text{BaFe}_2\text{As}_2$ . Interestingly, this compound

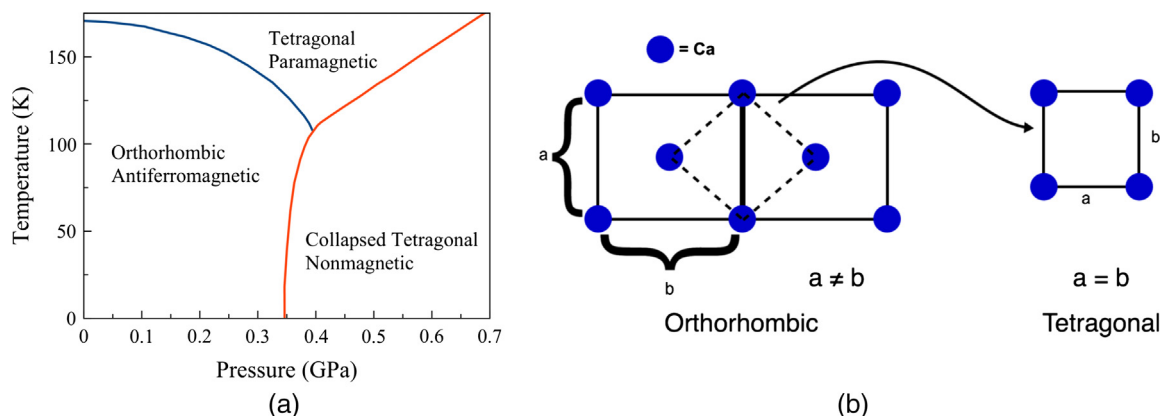
undergoes two phase transitions as a function of stress (uniaxial and hydrostatic) [20].

There have been a number of studies, both experimental and theoretical, that have attempted to both characterize and explain the observed phase transitions in  $\text{CaFe}_2\text{As}_2$ . Kreyszig et al. [21] conducted hydrostatic pressure experiments and reported that the orthorhombic to collapsed tetragonal phase transition at 50 K occurs at hydrostatic pressures of 0.3 GPa. Furthermore, they noted that at a fixed hydrostatic pressure of 0.63 GPa, there is a transition from the collapsed tetragonal to the tetragonal phase at 170 K. A study by Canfield et al. [13] explored these transitions further, and built the temperature-pressure phase diagram of  $\text{CaFe}_2\text{As}_2$  (Fig. 2a).

Initial density functional theory (DFT) simulations focused on the simulating the phase transition using constant pressure simulations and concluded the critical pressure was 5.3 GPa [8] at 0 K, dramatically higher than experiments. Colonna et al. [22] revisited the phase transition using a volume controlled simulation instead, and found the transition to be much closer to experiments, around 0.6 GPa. Widom et al. [23] conducted a similar investigation but argued that the phase transition was a first-order enthalpic transition, rather than being associated with an instability, with a reported phase transition pressure of 0.36 GPa. In addition, Tomic et al. [24] conducted uniaxial stress-controlled DFT simulations and demonstrated that the uniaxial stress required to drive the transformation was significantly less than the required hydrostatic stress, indicating that these compounds should be more susceptible to uniaxial loading. The theoretical work has demonstrated that there can be multiple interpretations of the cause of the phase transition, either an instability driven phase transition or an enthalpic one, and that the nature of the applied load will impact the response of these compounds.

In contrast to  $\text{CaFe}_2\text{As}_2$ ,  $\text{LaRu}_2\text{P}_2$  is non-magnetic and thus is unlikely to have a phase diagram as complex as  $\text{CaFe}_2\text{As}_2$ . Nevertheless, hydrostatic compression experiments have demonstrated nonlinearities in its mechanical response under pressure [12,25] which has been attributed to a tetragonal to collapsed-tetragonal transition [25]. DFT simulations have demonstrated that, in contrast to  $\text{CaFe}_2\text{As}_2$ , that there is no abrupt phase transition [9] and that the nature of the non-linear pressure-volume curves may have very different origins in  $\text{LaRu}_2\text{P}_2$  than in  $\text{CaFe}_2\text{As}_2$ .

The most recent experimental work by Sypek et al. [26,27] has investigated  $\text{CaFe}_2\text{As}_2$  under uniaxial loading and demonstrated a clear pseudo-elastic response of the material. These experiments also demonstrated that the phase transition can be induced by uniaxial loading along the  $c$ -axis and that it cannot be achieved by off-axis uniaxial compression. This work also opens up the possibility for this type of material to be used in mechanical applications where pseudo-elastic



**Fig. 2.** The pressure-temperature phase diagram of  $\text{CaFe}_2\text{As}_2$  [13] (a) shows the low-temperature, low-pressure orthorhombic phase, the high-temperature, low-pressure tetragonal phase, and the high-pressure collapsed tetragonal phase. (b) Upon the loss or randomization of the magnetic moments, the  $a$  and  $b$  axes of the orthorhombic unit cell will become equal in length, resulting in a transition to a tetragonal unit cell (viewed down the  $c$ -axis of the crystal).

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