

# Anomalies in nonstoichiometric uranium dioxide induced by a pseudo phase transition of point defects

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A uniform distribution of point defects in an otherwise perfect crystallographic structure usually describes a unique pseudo phase of that state of a nonstoichiometric material. With off-stoichiometric uranium dioxide as a prototype, we show that analogous to a conventional phase transition, these pseudo phases will also transform from one state into another via changing the predominant defect species when external conditions of pressure, temperature, or chemical composition are varied. This exotic transition is numerically observed along shock Hugoniot and isothermal compression curves in  $\text{UO}_2$  with first-principles calculations. At low temperatures, it leads to anomalies (or quasidiscontinuities) in thermodynamic properties and electronic structures. In particular, the anomaly is pronounced in both shock temperature and the specific heat at constant pressure. With increasing temperature, however, it transforms gradually to a smooth crossover and becomes less discernible. The underlying physical mechanism and characteristics of this type of transition are encoded in the Gibbs free energy and are elucidated clearly by analyzing the correlation with the variation of defect populations as a function of pressure and temperature. The opportunities and challenges for a possible experimental observation of this phase change are also discussed.

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## I. INTRODUCTION

Properties of states (or phases) of matter and the transformation between them are one of the central topics of modern condensed matter physics. When we speak of a phase or a state of matter, we are referring to a region of space in a thermodynamic system that is chemically uniform, physically distinct, and (often) mechanically separable. From a microscopic point of view, it usually constitutes a sequence of static or dynamic distributions of particles, which possess specific symmetry or ordering, and the physical properties are uniform, distinct, and time-independent in a statistical sense. It is widely used as a classification of matter, for example by differentiating them according to their state as solid, liquid, gas, or plasma, and subclassifying solids according to crystallographic symmetry, labeling magnetism by the ordering of magnetic moments, etc. When external conditions such as pressure, temperature, or chemical composition are varied, matter might change from one physical phase into another. This transformation is often accompanied by a sudden modification in crystalline structure or ordering state, and can be recognized by an abrupt change in thermodynamic properties. On the other hand, an abrupt change (or singularity) in derivatives of free energy—e.g., the specific volume, entropy, or specific heat—usually signals a reorganization of the particles, and thus can be used as a helpful indicator of phase transitions. Nevertheless, this is not always the case, especially in a complex system. In this paper, we will show that anomalous or quasidiscontinuous jumps take place in compression curves and other related thermodynamic quantities in nonstoichiometric uranium dioxide. These abrupt changes, however, do not correspond to any known physical phase transitions from a conventional point of view. Instead, we identify them as driven by a *pseudo phase transition* that is a result of a sharp switch of predominant defect species.

In principle, the introduction of defects might modify or tune the physical properties of a material. This modification,

however, is primarily a result of accumulation, and reflects the magnitude of defect concentrations. It is quite different from the abrupt variation in physical properties that arises from a symmetry or ordering change in a conventional phase transition. Therefore, according to the conventional classification, a defective state of a material cannot be labeled as a distinct physical phase compared with the perfect one. Notwithstanding this, in certain situations the defect concentrations are strictly constrained by, say, chemical composition, and thus it is possible that there will be a sudden change in predominant defect species when thermodynamic conditions are varied while keeping the underlying matrix structure almost unchanged. In this sense, a uniform distribution of each type of defect would have some distinct physical properties, and, analogous to a conventional phase transition, it might also lead to a jump in these properties when the predominant defect species is changed. We can therefore identify each such homogeneous distribution of defects as a *pseudo phase* according to the dominant species of defects to differentiate them. As will be shown below, at low temperatures the variation in defect population during a change of pseudo phases is very sharp, and strong anomalies or quasidiscontinuities in physical properties due to pseudo phase transitions can be expected.

## II. THEORETICAL MODEL

Uranium dioxide ( $\text{UO}_2$ ) is an important nuclear fuel. It is also a typical nonstoichiometric compound,<sup>1</sup> in which the structure of the underlying matrix (in fluorite structure here) is stable over a wide range of pressure and has a great degree of stoichiometry deviation. It thus serves as a good prototype to study the exotic effects of defects that manifest in thermodynamic properties. For this purpose, we first computed the energetics of a series of defective  $\text{UO}_2$  as a function of pressure to extract the contribution of defects to formation

free energies, from which defect populations as a function of temperature and pressure were then calculated. After this information was acquired, the Gibbs free energy as a function of chemical composition (or equivalently, the deviation of state (EOS) of the nonstoichiometric system as a derived quantity.

In particular, the total energy calculations of the defective  $\text{UO}_2$  system were carried out with the density functional theory using the projector augmented wave (PAW) pseudopotential<sup>2,3</sup> plus the plane-wave scheme as implemented in the VASP code.<sup>4,5</sup> The LSDA +  $U$  approach was employed to treat the strongly correlated  $5f$  electronic orbitals that are localized on uranium atoms, which splits the  $f$  band by an effective on-site Coulomb repulsion to form a Mott insulator state.<sup>6</sup> Details of the *ab initio* calculations, as well as the establishment of nonstoichiometric EOS, were given in Ref. 7. In particular, in order to eliminate electronic metastable states that are introduced via strong correlations of  $5f$  orbitals, we adopted the quasiaannealing method<sup>8</sup> to lower the electronic energy slowly by controlling the random disturbance from the ionic system, which acts as a kind of heat bath. Defect populations were evaluated using the point-defect model<sup>9-11</sup> and presumed a physical condition in the closed regime, which corresponds to the interior of a bulk material, and thus no exchange of particles with the exterior can occur.

### III. THERMODYNAMICAL ANOMALIES

With these calculations, an interesting phenomenon was observed in the hypostoichiometric regime ( $x < 0$ ) of  $\text{UO}_{2+x}$ . Figure 1 shows the Hugoniot that shocked from an initial condition of 500 K and 0 GPa for  $x = -0.02, -0.05, \text{ and } -0.1$ , respectively, by comparing with an isotherm of  $x = -0.1$  at 1700 K. A volume collapse was observed at about 39 GPa. Note that in calculations, we fixed the underlying matrix in a fluorite structure all the time, therefore this volume collapse does not correspond to any structural phase transformation. Nevertheless, this exotic behavior in the compression curve is very similar to what happens in a first-order phase transition.

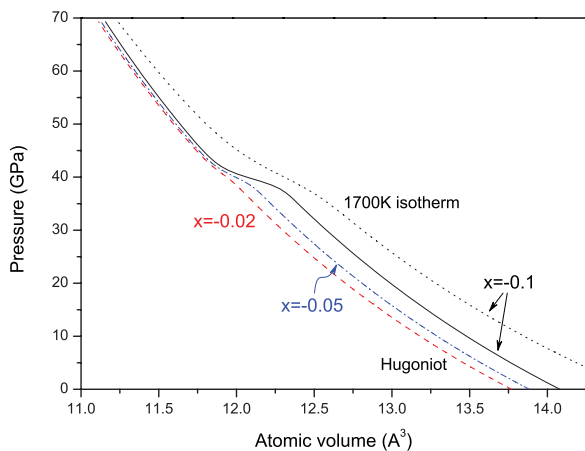


FIG. 1. (Color online) Compression curves of  $\text{UO}_{2+x}$  along the Hugoniot shocked from 500 K and 0 GPa as a function of the effective volume per atom at different stoichiometry deviations of  $x = -0.02, -0.05, \text{ and } -0.1$ , respectively. An isotherm of  $x = -0.1$  at 1700 K is also plotted for comparison.

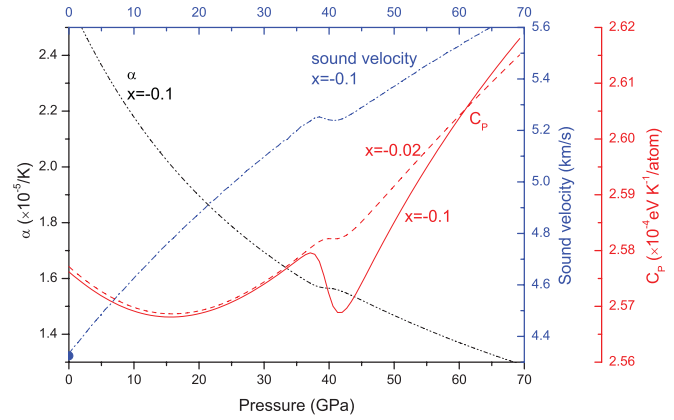


FIG. 2. (Color online) Anomalies in the thermal expansivity  $\alpha$ , isothermal bulk sound velocity, and specific heat at constant pressure  $C_p$  along the Hugoniot that shocked from 500 K and 0 GPa in nonstoichiometric  $\text{UO}_2$ . The solid circle (at the bottom left corner) marks the experimental bulk sound velocity measured at ambient conditions in perfect  $\text{UO}_2$ .

It is worthwhile to point out that the magnitude of this volume change is proportional to the size of the stoichiometry deviation  $x$ , which is more pronounced for  $x = -0.1$  than for  $x = -0.02$ . This is a direct consequence of the accumulation effect of defect populations, and is quite different from a first-order phase transition in which the dependence of the volume collapse on stoichiometry deviation should be weak. We also observed that the sharp volume change becomes smooth, and even less distinguishable, at higher temperatures, as the isotherm at 1700 K in Fig. 1 illustrates, which reminds us that it is not a conventional phase transition.

Furthermore, for nonstoichiometric  $\text{UO}_2$ , it is not only the compression curve that exhibits quasidiscontinuity; other thermodynamic quantities also manifest similar anomalies. Figure 2 plots the calculated thermal expansivity  $\alpha$ , specific heat at constant pressure  $C_p$ , and isothermal bulk sound velocity that defined as  $\rho C^2 = -V (\partial P / \partial V)_T$  along the same shock Hugoniot as in Fig. 1. Here  $\rho$ ,  $P$ ,  $V$ , and  $T$  denote the mass density, pressure, specific volume, and temperature, respectively. Experimental data of the bulk sound velocity of perfect  $\text{UO}_2$  measured at ambient conditions<sup>12</sup> are also illustrated for comparison. It can be seen that all of these thermodynamic quantities show a kink at the same pressure of about 39 GPa. It is interesting to note that the anomaly in  $C_p$  is much more striking than that of others, and is still discernible even for  $x = -0.02$ . By comparison, the expansivity  $\alpha$  already shows a nearly smooth crossover for  $x = -0.1$ , whereas at the same  $x$  the quasidiscontinuous change in sound velocity is just perceptible. The occurrence of quasidiscontinuity in both the first and second derivatives of the free energy at the transition point implies that although this transformation belongs to neither a first- nor a second-order phase transition, it has some features that are analogous to both of them.

In fact, the physical mechanism of this transformation and the associated anomalies are completely encoded in the construction of the Gibbs free energy of a nonstoichiometric system, which reads<sup>7</sup>

$$G(T, P, x) = G^0(T, P) + \Delta G(T, P, n), \quad (1)$$

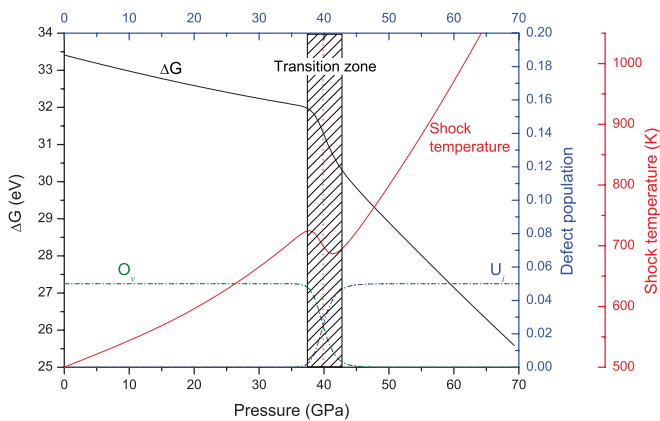


FIG. 3. (Color online) Variations of the shock temperature, defect populations, and the difference of Gibbs free energy with respect to the perfect  $\text{UO}_2$  when across the transition zone, respectively.

where  $G^0$  is the Gibbs free energy of the perfect system and  $\Delta G$  is that contributed by defects. The defect populations  $n$  are constrained by the composition equation of

$$f(n_1, n_2, \dots, n_i) = x. \quad (2)$$

To the first-order approximation,  $G$  can be written as

$$G \approx G^0 + \sum_i \delta G_i n_i. \quad (3)$$

Since the  $\delta G_i$ 's differ from each other, the Gibbs free energy thus could have a crossover when the predominant defect switches from one type to another under a variation of external conditions of temperature, pressure, or chemical composition. Furthermore, since the distribution of point defects satisfies Boltzmann statistics, the population variation is in proportion to  $\exp(-\delta G/k_B T)$ . Therefore the crossover is smooth at high temperatures but becomes sharp at low enough temperature, which leads to a discontinuity or strong anomaly in thermodynamic properties. It is necessary to note that since the Gibbs free energy in Eq. (3) is analytic, all of its derivatives must be continuous at finite temperatures, even though some of them might appear to be *quasidiscontinuous*.

Figure 3 shows the variation of shock temperature of  $x = -0.1$ , in which the kink is much more appreciable than in the  $P$ - $V$  curve. Also, the difference of the Gibbs free energy with respect to the perfect  $\text{UO}_2$  (i.e.,  $\Delta G$ ) and the defect populations as a function of shock pressure are plotted. It can be seen that the kink in temperature corresponds exactly to the point of switch of predominant defect species. At low pressure it is oxygen vacancy ( $\text{O}_v$ ) that dominates. But at a pressure higher than 39 GPa, uranium interstitial ( $\text{U}_i$ ) starts to take over, and  $\text{O}_v$  is suppressed completely. This switch is also reflected in the Gibbs free energy as a function of shock pressure, and  $\Delta G$  (i.e., that contributed by defects) displays a clear crossover from one end to the other when crossing the transition zone. These demonstrate that the anomalies are the result of a pseudo phase transition in nonstoichiometric  $\text{UO}_2$  driven by compression, as the above discussions implied.

If we define the locus of the intersection points of defect populations (usually at the transition zone center) as a pseudo phase boundary, a pseudo phase diagram can be

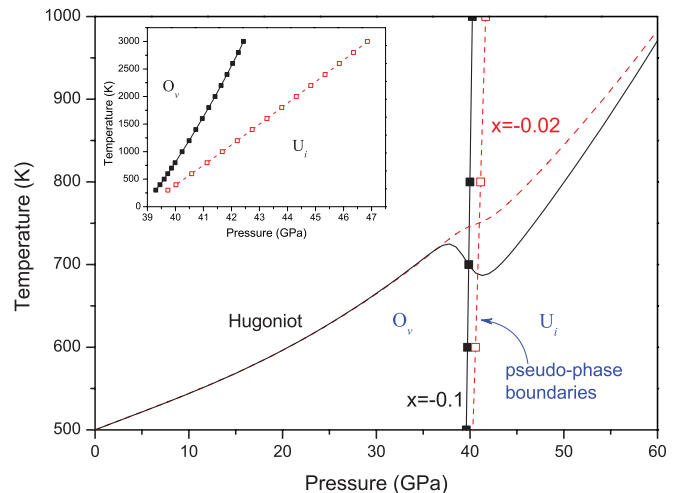


FIG. 4. (Color online) Pseudo phase diagram of hypostoichiometric  $\text{UO}_2$  on the  $T$ - $P$  plane, together with the induced anomaly in shock temperature. Solid lines denote that for  $x = -0.1$  and dashed lines for  $x = -0.02$ . Inset provides an overall view of the boundaries that separate the dominant defects of oxygen vacancy and uranium interstitial for  $x = -0.02$  (open square) and  $-0.1$  (filled square), respectively.

constructed, which divides the dominant regime of different defect species. As shown in Fig. 4, for hypostoichiometric  $\text{UO}_2$ ,  $\text{O}_v$  dominates the low-pressure region and  $\text{U}_i$  is the main defective component at high pressures. Also, we found that decreasing  $x$  increases the transition pressure slightly. The change is about several giga-pascal at high temperatures, but less than 1 GPa when below 500 K, as the inset of Fig. 4 shows. Overall, the temperature dependence of the pseudo phase boundary is weak, reflecting the fact that this transition is mainly driven by compression.

It is worthwhile to point out that the width of the transition zone increases with temperature. This is a direct reflection of the dependence of defect populations on temperature. At a high enough temperature, the transition zone will become so wide that the crossover behavior is almost indiscernible, and then the quasidiscontinuities (or kinks) in thermodynamic quantities disappear. On the other hand, it should be noted that theoretically a pressure-induced pseudo phase transition at absolute zero Kelvin is possible, which, however, requires a large zero-point motion of particles to facilitate ionic diffusion in order to make the switch of defect species possible. In this extreme case, the width of the transition zone becomes zero, and the Gibbs function has a sharp kink so that all of its derivatives become truly discontinuous at the transition point. It looks more like a first-order transition. The difference is that all derivatives of the free energy higher than the first order are divergent at the transition point for a first-order phase transition, while they are finite for a zero Kelvin pseudo phase transition. This difference comes from the fact that for a defect-type switch transition, the derivatives are carried out with defect populations being fixed, which is well defined even at the transition point. But this is not the case for a first-order phase transition, and only the left (or right) limit can be defined. Figure 5 illustrates the characteristic of evolution of the crossover from being quasidiscontinuous at low temperatures

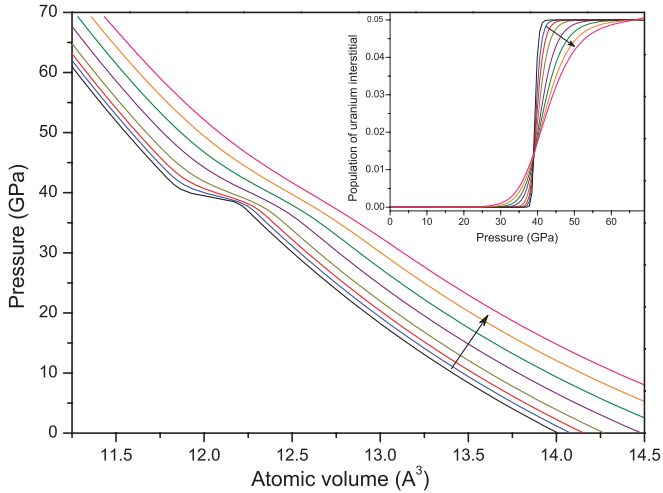


FIG. 5. (Color online) Isothermal compression curves for  $x = -0.1$  at temperatures of 300, 500, 700, 1000, 1500, 2000, 2500, and 3000 K, respectively. Inset: defect population of uranium interstitial along the isotherms. Arrows indicate the direction of temperature increase.

to a smooth bridging at high temperatures. The variation of the population of  $U_i$  as shown in the inset of Fig. 5 as a function of pressure and temperature, which exhibits a sharp jump at low  $T$  but becomes a smooth crossover at high  $T$ , explains perfectly all anomalous behavior observed in the Gibbs free energy and its derivatives.

#### IV. DISCUSSION AND CONCLUSION

In the above discussion, we did not consider the possibility of a phase segregation, or equivalently, the stability of hypostoichiometric  $UO_2$ . Experiments indicated that the stable range of  $x$  at low temperature is very narrow, especially in the  $x < 0$  side.<sup>13,14</sup> Nevertheless, a metastable  $UO_{2+x}$  with  $x = -0.02$  had been successfully synthesized at room temperature in the laboratory.<sup>15</sup> Although the above discussions showed that the anomalies for this chemical composition are weak in the specific volume or shock temperature, a kink in the  $C_P$  curve is still evident, which implies that the pseudo phase transition can be detected by a highly accurate measurement of  $C_P$  in  $UO_{1.98}$ . Furthermore, it is also possible that a metastable phase with  $x = -0.05$  can be synthesized at high temperatures. This stoichiometry deviation would provide more noticeable anomalies, and thus it is much easier to detect. In addition, according to the phase diagram of  $UO_{2+x}$ , when temperature is higher than 1000 K, a composition of  $x = -0.1$  might become possible. At this temperature range, the crossover behavior should have been obscured drastically, but our calculations indicate that some of the thermodynamic properties, especially  $C_P$ , still exhibit a strong anomaly that can be detected by experiment.

Another challenging issue for experiments to detect a pseudo phase transition is the possible interference coming from structural transition of the underlying matrix. Our calculations suggested that the pseudo transition in  $UO_{2+x}$  might take place at about 39 GPa at room temperature. For perfect  $UO_2$ , however, compression also leads to a phase transition from fluorite structure to cotunnite phase at  $\sim 42$  GPa.<sup>16,17</sup>

Considering that the introduction of defects should weaken the stability of the matrix, the actual transition pressure of the underlying matrix for the off-stoichiometric compound thus might be lowered to overlap with that of the pseudo phase transition and make the relevant experiments very difficult. Nonetheless, what we considered here are only neutral defects. Since  $UO_2$  is an insulator within this pressure range, the defects can be charged. This would modify the energetics of all defects.<sup>18</sup> Therefore, there is still the possibility that the  $O_v-U_i$  switch occurs at a much lower pressure. To make a reliable assessment of this, however, a comprehensive evaluation is required of the energetics of charged defects in  $UO_2$ , which is beyond the scope of this paper. In spite of that, our analyses definitely demonstrated that a pseudo phase transition is practically possible in nonstoichiometric compounds.

According to the defect-type switching mechanism, a pseudo phase transition driven by temperature or chemical composition rather than by compression is also possible. Similar anomalies can be expected for all of these transitions. In fact, the anomalies in the thermal expansion coefficient and the bulk modulus due to defect-type switch might have been observed experimentally in  $Fe_{1-x}O$ . A large discontinuous jump in thermal expansivity and bulk modulus was observed when the chemical composition went beyond the point of  $Fe_{0.98}O$ .<sup>19,20</sup> The underlying physical mechanism was not clearly understood at that time, and it was proposed that it might be related to defect clustering as  $x$  increased. It becomes clear now that this picture is perfectly in line with the pseudo phase transition just discussed above if we treat the defect clusters as independent species, i.e., it is the switch of defect species that leads to the observed quasidiscontinuous jump in thermodynamic properties. Furthermore, we noticed that the transition in  $Fe_{1-x}O$  is very similar to what would happen in a hyperstoichiometric  $UO_2$ , where the stoichiometry deviation drives a transition from point oxygen interstitial to  $COT-o$  cluster, as the pseudo phase diagram of Fig. 3 in Ref. 21 implied. However, it should be noted that it is difficult to control the stoichiometry deviation continuously, thus it is still very important to study by experiment the pseudo phase transitions that are driven by pressure, which can provide a more explicit and clear-cut physical picture.

In summary, we showed in this paper that a pseudo phase transition can occur in nonstoichiometric compounds (and alloys as well). It arises from a rapid switch of predominant defect species driven by external conditions of pressure, chemical composition, temperature, and so on. At high temperatures, this transition is a smooth crossover, whereas it becomes quasidiscontinuous at low temperatures and has features similar to a first-order phase transition. A real discontinuity might be possible at 0 K, but it requires a large zero-point motion of ions to facilitate particle diffusion, therefore it is only possible in compounds of light elements. Being analogous to a physical phase transition, anomalies are also present in thermodynamic properties at the transition point of a pseudo phase transformation. With hypostoichiometric  $UO_2$  as a prototype, we demonstrated that such anomalies are evident in both shock Hugoniot and isothermal compression curves using *ab initio* calculations. The transition mechanism was clearly elucidated by analysis of the Gibbs free energy



and evolution of defect populations as a function of pressure, stoichiometry deviation, and temperature. We also discussed the possibility to observe this transition in nonstoichiometric  $\text{UO}_2$  by experiment, as well as the accompanying challenges. It is worthwhile to point out that since electronic structure and magnetic property are usually governed (or tuned) by defect species, a pseudo phase transition thus indicates a rapid change of these properties (in addition to the thermodynamic properties that are direct derivatives of the Gibbs free energy). In this regard, the effect of a pseudo phase transition of defects

might have potential impacts on electronic applications, for example in pressure-sensitive switchers that change the electronic state of a device from one state to another by slightly adjusting the stress state.

#### ACKNOWLEDGMENTS

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