Atomistic simulation of a superionic transition in fluorite type structures UO$_2$, UN$_2$, TiH$_2$

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Abstract. The results of the atomistic simulation of a superionic transition and melting of stoichiometric UN$_2$, UO$_2$ and TiH$_2$ have been presented. Simulation shows that superionic transitions of UO$_2$ and TiH$_2$ take place at temperature below melting temperature, while UN$_2$ did not show such feature. This difference in properties of studied structures is caused by various gap between formation energies of Frenkel pair defects for sublattices. The possibility of describing the superionic transition within the theory of second-order phase transitions has been discussed, the conditions of the existence of superionic transition have been discussed.

1. Introduction

It is known that fluorite-type structures can show superionic transition at temperatures close to melting. In particular, superionic transition in UO$_2$ has been discussed in various works [1–3]. The presence of this transition can be explained by the ability of anion sublattice to accumulate defects and cation capability to adapt the valence to the given anion defect configurations [4]. This process is characterized by the high growth of electric and heat conductivity. Since 1990 there were series of experiments and calculations that proved the existence of such transition in some of fluorite structures. But there is still a number of fundamental questions: whether the superionic transition actually can be considered as a phase transition; to which type this phase transition belongs; what the necessary conditions for this transition are and if it is possible to predict such transition in structures of a different type except fluorite. So far, there is no evidence to suggest that the superionic transition can be observed in all the structures of the fluorite type. There are certain difficulties in constructing of theory of superionic transitions. Nevertheless, the mechanism of this transition in fluorites is well known—the phenomenon is provided by the growth of concentration of point defects in anion sublattice. Detailed discussion of the theoretical description of superionic transition in UO$_2$ was presented in works [4–6].

Different approaches to describe this transition theoretically may be used. In [5] this problem is studied within the framework of Landau theory of phase transitions. Using this theory it is possible to explain the anomalous temperature dependency of heat capacity and diffusion coefficient. One of the basic characteristics in this approach is the order parameter, which describes the value of defects concentration. Taking into account defects interaction as well as cation sublattice field and symmetry of a crystal, it is possible to construct...
Hamiltonian of a system (Landau Hamiltonian). It has been shown that experimentally obtained
temperature dependency of diffusion coefficient may be approximated from consideration of
Landau Hamiltonian [5].

Another approach, based on statistical thermodynamics, has been demonstrated in [4].
It should be highlighted that authors provide research on nonstoichiometric $\text{UO}_2\pm x$ and
stoichiometric solid is treated as a special case. The main idea is the derivation of an equation
for Helmholtz free energy for non-ideal solid, containing Frenkel defects. In this case, the
contributions in free energy of ideal solid are the result of Coulomb and short-range (which is very
much like dipole-dipole interaction) defect interaction and short-range repulsion forces (which
accompany displacements of ions). Equations for thermodynamic parameters of a system were
derived from the free energy equation using standard thermodynamic relations. The obtained
equations reproduce $\lambda$-temperature dependences of heat capacity and thermal expansion in
stoichiometric case. The results of theoretical computations for nonstoichiometric $\text{UO}_2+x$ were
compared with experimental data and showed good agreement.

The two mentioned above approaches show how the disordering of anion atoms influence
anomalous behavior of heat capacity of a crystal during superionic transition. Moreover, both
considerations [4, 5] show us that in stoichiometric $\text{UO}_2$ it is a second order phase transition.
In hyperstoichiometric compositions the second model predicts a “diffuse transition”, but not
$\lambda$-transition.

In this work we have verified the presence of superionic transition and melting in $\text{UO}_2$, $\text{UN}_2$
and $\text{TiH}_2$. Both transitions can be observed in $\text{UO}_2$ and $\text{TiH}_2$ while $\text{UN}_2$ shows only melting at
equilibrium simulation. As a result of our research, we provide essential conditions for possibility
of superionic transition in stable state. In addition, we have found that superionic transition
can be observed in metastable $\text{UN}_2$, i.e. upon fast heating.

2. Computational technique
The investigation was carried out using the molecular dynamic method which is powerful tool
for study of structure/phase transition [7, 8]. Details of simulation were previously presented
in work [9]. For $\text{UO}_2$ we used pair potential MOX-07 taken from [10, 11]. For $\text{UN}_2$ we used
angle depended potentials (ADP) from work [12], which was created by force-matching method.
For $\text{TiH}_2$ we used modified version of ADP from work [13] with minor changes in development
procedure.

The simulated systems consisted of 21000 atoms. The calculation was performed with periodic
boundary conditions. The step of the integration over the time for the Newton’s equations was
0.5 fs. The calculations simulated the slow heating of the system at a fixed pressure or at a fixed
volume. The changes of thermodynamic characteristics caused by the heating of a solid were
studied. Therefore, depending on a particular task, we used either $NVT$-ensemble or $NPT$-
ensemble. The temperature and pressure were controlled using the Langevin thermostat and the
Nose–Hoover barostat, respectively. The duration of the calculations was approximately 5 ns.
To calculate the melting curves, we used the direct two-phase simulation [7,14,15]. In addition,
we used energy minimization method for calculation of the formation energies of Frenkel pair
defects. All the calculations were performed with the LAMMPS code [16], and the visualization
of the atoms dynamics was carried out with the Atom-Eye program [17].

3. Fluorite structure
The investigated materials have the fluorite-type structure. It means that uranium and titanium
atoms form a face-centered cubic lattice, but oxygen, nitrogen and hydrogen atoms form a simple
cubic lattice. The lattice parameter of the last sublattice is two times smaller than of the first
one. This structure provides possibility for light atoms to jump from usual “site” positions
into the “interstitial”, as shown at figure 1. For some fluorites this process takes place at the
Figure 1. Structure of UO$_2$. The gray circles indicate the positions occupied by the oxygen atoms in the conventional crystal lattice, U is the site position of the uranium atom, O is the site position of the oxygen atom, and O$_I$ is the interstitial position of the oxygen atom.

temperature some smaller than melting one. So, one can observe so-called superionic transition described above. But the atoms’ arrangement is not the single factor for such process.

4. Results

4.1. Generation of point defects during superionic transition in UO$_2$

To clear the mechanism of superionic transition we have investigated the process of accumulation of point defects. As it was mentioned above, this process can not be observed in equilibrium stoichiometric UN$_2$. The details and the results obtained for UO$_2$ are considered below.

To examine accumulation of defects we have simulated the heating process of UO$_2$ from $T = 1500$ K to $T = 3500$ K. Point defects in oxygen sublattice appear at temperatures a little higher than 2000 K. U-sublattice remains crystalline without any defects at this temperature range, as it is shown at figure 2. We have counted the point defects’ density $N_{FP}$ at certain temperatures $T$. The figure 3 shows the result of these calculations for two values of lattice parameter. In our terms $N_{FP}$ means the ratio of the number of interstitial atoms (or Frenkel pairs) to the total number of atoms of this type (oxygen).

The simulation shows that oxygen defects occur in the whole volume of the simational box, i.e. there is no nucleation during superionic transition. The density of defects grows as $T$ increases, but achieves maximum (about 0.15-0.2) at the transition temperature $T_c$, which is smaller than the melting temperature $T_m$. This value of defects density remains the same up to the melting temperature. We can suppose, that the accumulation of point defects in our case takes place according to Frenkel [18, 19]:

$$ N_{FP} = \exp \left( \frac{S_{FP}}{2k} \right) \exp \left( - \frac{H_{FP}}{2kT} \right), $$

where the entropy of Frenkel pair formation $S_{FP}$ usually ranges from 5$k$ to 12$k$ [18]. At low pressures the enthalpy of formation $H_{FP}$ is approximately equal to the energy of formation $E_{FP}$, which can be calculated as

$$ E_{FP} = E_{\text{def}} - E_{\text{id}}, $$
Figure 2. Fragments of the atomistic simulation (projection of the atomic positions onto the $xy$-plane). Snapshots are corresponded to the states with different temperatures: (a) $T = 1500$ and (b) $T = 2900$ K. The oxygen and uranium sublattices are shown at the left and right, respectively.

Figure 3. Density of Frenkel pairs in the oxygen sublattice at different temperatures: 1 and 2—points obtained by the simulation in an NVT-ensemble for two different lattice constants (0.540 nm and 0.537 nm); 3—theoretical dependence (1) for $E_{FP} = 3.7$ eV.

where $E_{def}$ and $E_{id}$ are the energy of a system with a Frenkel pair in the oxygen sublattice and the energy of an ideal system without any defects, respectively.
To verify dependence (1), we have made accurate calculations of the formation energy of Frenkel pair defect, using the method of energy minimization. This calculation gave us \( E_{FP} = 3.7 \) eV for O-defects in UO\(_2\). We also estimated \( S_{FP} = 9k \). This gave us opportunity to obtain a theoretical dependence of point defects density. The corresponding line is presented at figure 3 (line 3). As it can be seen, at the beginning of transition (i.e. at low defects density) the temperature dependence of point defects can be described by the Arrhenius equation (1) with \( E_{FP} = 3.7 \) eV. At temperatures close to \( T_c \), the \( N_{FP} \) is higher than the value calculated from equation (1). Apparently, this difference is explained by the interaction of defects with each other, which decreases the formation energy of a defect, while \( E_{FP} = 3.7 \) eV corresponds to calculations, in which we simulate occurrence of defects in the lattice without others defects.

The simulation of heating of TiH\(_2\) shows that all the findings discussed above are also correct for this structure. We can define the temperature of superionic transition \( T_c \) as the temperature at which defects density achieves threshold value \( N_{FP}^{th} \) (i.e. maximum value). Dependence (1) allows us to estimate the temperature of the superionic transition

\[
T_c = \frac{E_{FP}}{2k} \left( \frac{S_{FP}}{2k} - \ln N_{FP}^{th} \right)^{-1}.
\]

4.2. Changes in thermodynamic characteristics in the superionic transition

In this part of the work we consider the temperature dependencies of pressure, potential energy, heat capacity and coefficient of thermal expansion. The calculations were held for all three simulated structures. The temperature changed in a wide range up to melting temperature. Moreover, we held simulation with fast heating for UN\(_2\) up to the metastable superheated solid, because only in this case we observed phenomenon similar to a superionic transition.

The simulation showed that superionic transition in UO\(_2\) and TiH\(_2\) is characterized by continuous changes of pressure \( P \) and energy with increasing of \( T \) and leaps in heat capacity \( C_p \) and coefficient of thermal expansion \( \alpha \) [6,9,20]. The continuous character of \( P(T) \) dependence means that the volume of a system remains the same during superionic transition. All these facts let us suppose that the superionic transition may be described by the theory of second-order transitions. It is known that the pressure dependence of the transition temperature in case of a second-order phase transition is described by the Ehrenfest equation

\[
\frac{dT_c}{dP} = P \left[ (\partial \tilde{V} / \partial T)_{P} C_p \right],
\]

where \( \tilde{V} \) is the molar volume of the system and the operation \([\ldots]\) denotes a change during the phase transition. For \( (\partial \tilde{V} / \partial T)_{P} \) and \( C_p \) these changes were calculated directly [9]. Using the calculated values of \([C_p]\) and \([(\partial \tilde{V} / \partial T)_{P}]\), we can compute the slope of the curve of phase transition on the \( P-T \)-diagram. Thus, the theoretical estimate of \( dT_c/dP \) obtained in this work for UO\(_2\) is equal to \( 10 \pm 5 \) K/GPa. The large error is explained by the error in the calculation of the \( T_c \).

We also have made direct calculations of the dependence of \( T_c(P) \). In addition, we have obtained the melting line of UO\(_2\) using two-phases type of simulation. The results of simulations are shown in figure 4. This direct calculation of \( dT_c/dP \), according to the simulation results (figure 4), gives the value of \( 7 \pm 2 \) K/GPa, which agrees well with the estimate obtained from the Ehrenfest’s equation. Using the same method for TiH\(_2\) we have found \( T_c = 1000 \) K at zero pressure and \( dT_c/dP = 4 \pm 1 \) K/GPa.

To make sure that we deal with equilibrium heating, we have carried out simulations of heating of studied solids in the same temperature interval, but with various heating rate. For UO\(_2\) and TiH\(_2\) the obtained dependencies \( P(T) \) and \( E(T) \) are independent from heating rate. It means that our calculations were slow enough so that the process was not metastable.
4.3. Phase diagrams of UN₂

The melting curve for UN₂ was calculated using the atomistic two-phase simulation. The figure 5 shows the arrangement of atoms at melting temperature of UN₂ during two-phase simulation. In this case both sublattices melt simultaneously. Further it will be shown that this distinction in properties of UN₂ from other simulated structures is caused by different values of ratio of formation energies of Frenkel pairs for sublattices in these structures.

We have found that superionic transition can be observed in metastable UN₂, i.e. upon fast heating. In this case, the generation of defects is described by (1), but \( T_c > T_m \). The calculated phase diagram is shown at figure 6. We see that for UN₂ the melting curve lies below the superionic curve. This means that superionic transition may be observed in metastable zone. So we must somehow avoid melting of a system to get superionic transition. In our case we heat our system so fast that it does not melt during heating.

5. Discussion

The fact that UO₂ and TiH₂ show superionic transition in stable state and UN₂ only in metastable state helped us to manifest one of the required factors of possibility of superionic transition. We compared formation energies of Frenkel pair for both sublattices in all three systems which are calculated by energy minimization method. The results are presented at table 1. As it can be seen, \( E^{O}_{FP} \ll E^{U}_{FP} \) and \( E^{H}_{FP} \ll E^{Ti}_{FP} \) for UO₂ and TiH₂, but \( E^{N}_{FP} \sim E^{U}_{FP} \) for UN₂. This is the reason why U-sublattice in UN₂ loses order at the same temperature as N-sublattice if we allow our system to relax during heating (i.e. melting occurs). For UO₂ and TiH₂, O- and H-sublattices require smaller temperatures to generate defect, than U- and Ti-sublattices respectively, so we can observe superionic transition. The necessary condition \( E^{A}_{FP}/E^{B}_{FP} < 0.5 \) may be used for estimation of superionic transition possibility in A-B binary system [9].
Figure 5. Fragments of the atomistic two-phase simulation of UN$_2$ (projection of the atomic positions onto the $xy$-plane). Snapshots are corresponded to equilibrium state at melting temperature. The uranium and nitrogen sublattices are shown in (a) and (b) figures, respectively.

Figure 6. Phase diagram of UN$_2$: 1—calculated melting line; 2—estimation of superionic transition curve.

Another interesting result is the verification of equation (3) for simulated systems. We have plotted dependence $T_c(E_{FP})$ using data from the simulations. We consider $S_{FP} = 9k$ and $N_{FP}^{th} = 0.04$ (see discussion in [9]). The slope of theoretical curve $T_c(E_{FP})$ is equal to 750 K/eV and this value agrees well with direct calculation (figure 7).
Figure 7. The dependence of temperature of superionic transition $T_c$ on $E_{FP}$ for simulated materials: 1—TiH$_2$, 2—UN$_2$, 3—UO$_2$. The line corresponds to equation (3).

Table 1. Formation energies of Frenkel pair defects in $A$–$B$ binary system. The calculation was performed by the method of energy minimization.

|          | UO$_2$ | UN$_2$ | TiH$_2$ |
|----------|--------|--------|---------|
| $E_{FP}^A$ for O, N and H | 3.7    | 2.4    | 0.9     |
| $E_{FP}^B$ for U and Ti  | 14.4   | 3.5    | 6.2     |
| $E_{FP}^O < E_{FP}^U$ | $E_{FP}^N \sim E_{FP}^U$ | $E_{FP}^H < E_{FP}^{Ti}$ |

6. Conclusion

The atomistic simulation of heating of the stoichiometric fluorite-type structures UO$_2$, UN$_2$ and TiH$_2$ showed that the way atoms are arranged in this structure is not enough to provide superionic transition. One of the required factors is the low ratio of formation energies of Frenkel pair defects of sublattices $E_{FP}^A/E_{FP}^B$. For UO$_2$ and TiH$_2$ these ratios are approximately 1:4 and 1:7, respectively. It can be expected that in other ordered binary systems with the same or lower ratio the superionic transition can be observed. It has been found that the accumulation of defects during the superionic transition can be described by the Arrhenius equation. At high values of defect concentration the interaction between atoms in usual sites and interstitial should be taken into account as it decreases the energy of Frenkel pair formation.

It was shown that during superionic transition pressure and energy grow continuously in respect to temperature, while heat capacity and coefficient of thermal expansion have leaps. Defects appear in the whole volume without nucleation. Superionic curve on $P$–$T$-diagram may be described by Ehrenfest equation. For UO$_2$ and TiH$_2$ it was shown that the superionic transition appears upon equilibrium heating and can be described in the framework of the theory of second order phase transitions.
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