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Defect Formation Mechanisms and Point Defect Concentrations in the Anion Sublattice of Uranium Dioxide: Molecular Dynamics Study

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Abstract. Anion defect concentrations in the uranium dioxide were calculated in a wide temperature range by the molecular dynamics (MD) method, and a good agreement with the neutron scattering experimental data is shown. Groups of isolated interstitial anions with the absence of anion vacancies in N nearest neighborhoods ($N=1-4$) were extracted, formation energies of each group in the different phase states were derived.

The formation energy of anion defects 4eV, derived by the MD method at low temperatures, in general coincides with the experimental estimations (3–4)eV and the lattice static results 4.1eV, using the same interaction potential. At high temperatures in the superionic state anion Frenkel defects (with $N=3,4$) have negative formation energy of about (-14)eV, concentrations of these defects are very small compared with the total defect concentration, including non-stoichiometric crystals. The validity of the point defects model in the superionic state and transition regions is also discussed.

The model of anion diffusion via the formation of short-living pairs "vacancy–interstitial anion" is proposed and confirmed by MD calculations. It is shown that in the superionic state the exchange mechanism dominates, and at low temperatures it coexists with the diffusion via the formation of long-living anion Frenkel pairs.

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Key words: Molecular dynamics, uranium dioxide, defect concentration, exchange diffusion, superionic state, point defects model.

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1 Introduction

The anion sublattice of the uranium dioxide and its structural analogues – cerium, plutonium, zirconium dioxides, as well as various fluorides and chlorides with the fluorite-type structure, was extensively studied over recent decades. The temperature regions of the crystalline state, the superionic (SI) transition and the SI state were explored in detail by experimental measurements of the electric conductivity or oxygen isotopic diffusion measurements, as well as by the neutron scattering investigations. The formation and migration energies of anion Frenkel (AF) defects were calculated by the lattice statics and *ab initio* methods, whereas calculations of the diffusion coefficients were carried out by the molecular dynamics (MD) method. A thermodynamics point defects model was developed and is used for the interpretation of experimental data and to predict the behavior of materials during a long time operation under different conditions.

The results of experimental and theoretical researches have a poor agreement with each other. Former MD calculations of anion vacancy concentration in the SI state (2-3)% [1–3] diverge from the experimental results of neutron scattering (35-45)% [4–7], as was also noted in [8]. The formation and migration energies of anions, calculated by the lattice statics method, generally coincide with the experimental values, but this is not the case for the activation energies calculated from MD. Moreover, for a given interaction potential the anion diffusion activation energy from MD significantly differs from the value, calculated based on the AF defect formation energy and the anion migration energy values, derived by the lattice statics, if one uses the standard point defects model [9]. According to the widely used Lidiard and Matzke approximation [10], anion defects affect the formation energy of cation defects. Cation sublattice affects the stability of the material and determines technological parameters such as creep, crack growth and similar mechanical properties. To predict the cation sublattice behavior at high temperatures the AF pair formation energy is often simply assumed to be zero in the Lidiard and Matzke model, but this assumption also should be verified.

The purpose of the first part of this study is the precise calculation of concentrations of anion vacancies and interstitial anions in a wide temperature range, especially at temperatures close to the melting point, where the mobility of anions is extremely high. Groups of interstitial anions without anion vacancies in direct neighborhood will be studied individually. A comparison is then possible with the classical point defects model, in which an AF pair is defined as a vacancy and an interstitial anion, separated by an infinite distance. From the temperature dependence of concentrations of vacancies and interstitial anions groups the formation energies of AF pairs of different types can be derived and compared with the experimental and lattice statics results.

The diffusion of anions in stoichiometric uranium dioxide and its structural analogs can occur not only by anion Frenkel disorder, but also via the so-called exchange mechanism. The exchange diffusion and its contribution to the overall mobility of anions will be investigated in detail in the second part of this study. In this work a model of the diffusion based on the formation of short-living local pairs "anion vacancy–interstitial anion"