



Modelling of high temperature superionic transition of uranium dioxide crystals

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Abstract

A microscopic model of the high temperature ($T \approx 2670$ K) phase transition of uranium dioxide crystals to the super-ionic state is developed. It is shown that the self-consistent consideration of the point defects and the electron subsystem interactions (leading to additional strong screening of the defect charges) in the 'mean-field' approximation and the real symmetry of the UO_2 crystalline lattice afford satisfactory agreement of the model calculations with experimental data on the degree of the anion sublattice disorder and an anomalous behaviour of the specific heat of uranium dioxide in the given temperature range. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Considerable efforts in experimental and theoretical investigations of the high-temperature behaviour of uranium dioxide were gained during the last years. This problem is of great interest both from a practical point of view (the behaviour of the nuclear fuel during an accident temperature escalation) and for purely theoretical reasons. For example, the problem of an adequate microscopic description of the anomalous thermodynamic behaviour of the UO_2 crystals at temperatures $\approx 0.8T_m$ near the melting point T_m remains still open. The significant peak in the specific heat and the steep increase of the anion sublattice disorder in the temperature range of $\approx 100^\circ\text{C}$ in the vicinity of this peak are assigned to the so called 'Bredig transition'. Such a behaviour is usually associated with the superionic transition which was observed in other crystals with fluorite structure over the same temperature range (close to $0.8T_m$).

In early investigations (see, for example, Ref. [1]) the specific heat growth was connected solely with the electron subsystem excitations taking into account that uranium dioxide is a semiconductor with a wide energy

gap of about 2 eV. Later this anomaly was mainly attributed to the anion subsystem disordering which was described in the framework of the lattice gas model. Thus Tam et al. [2] took into account the ionic nature of the UO_2 crystal and also considered the electric charge of generated point defects. In this case the long-range Coulomb interactions between the charged defects screened by the Debye–Hückel mechanism give a significant contribution to the free energy of the system. Such a screening strongly diminishes the formation energy of the Frenkel pairs when some critical concentration of defects is attained during the temperature rise. This may result in the substantial spontaneous increase of the defect generation. Initially such a mechanism of the superionic transition in the fluorite type crystals was proposed by March et al. [3]. However, the repulsion of the defects of one sort is not screened at interatomic distances and thus is rather strong. For this reason, the 'blocking' of the neighbouring sites occupied by similar defects has to be taken into account. Such a consideration performed in the model [2] led to an abrupt increase of the equilibrium defect concentration at sufficiently high temperatures and qualitatively improved the description of the phase transformation mechanism. However, the quantitative results were still in a remarkable contradiction with available experimental data. Indeed, the critical defect concentration determining the onset of the superionic transition was

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calculated in Ref. [2]: $n \approx 3 \times 10^{-3}$. This value was considerably lower than the value $n \approx 0.1$ measured by Hutching [4] by neutron scattering.

For a more exact quantitative description of the superionic transition in the crystal with the fluorite structure a series of microscopic models of lattice gas type were proposed, which treated this problem in the mean-field approximation. These models described the Frenkel defect distribution over two sublattices taking into account long-range interactions, and differed among themselves by the introduction of various terms in the free energy functional specifying the configurational entropy of the defects. The emerging anomaly in the specific heat could be successfully explained by an appropriate choice of these terms, however, such a procedure had an artificial character. For example, in Ref. [5] an additional term specifying the vibrational entropy of defects and proportional to $\ln(\omega_i/\omega_0)$, was introduced in the free energy functional (where ω_i and ω_0 are the vibration frequencies of oxygen atoms in interstitial and regular lattice sites, respectively). However, the ratio of these frequencies which furnished a coincidence of results of the model [5] with experimental data for the behaviour of the equilibrium defect concentration near the transition temperature appeared to be unjustifiably high: $\omega_i/\omega_0 \approx 10^2$ (compare, for example, with Ref. [6]). In Ref. [7] in order to consider the blocking of neighbour sites occupied by charged defects, the number of possible sites in the sublattices was expressed as an unknown function of the defect concentration with some fitting parameters, and so on.

In that situation a more general (phenomenological) consideration, which allowed a correct description of the symmetry and form of the free energy functional in the vicinity of the transition, seemed to be important. Such an approach was realised within the framework of the Landau theory of phase transitions by one of the present authors in Refs. [8,9]. Based on the general symmetry consideration of the fluorite-type crystals, this theory allowed the determination of the nature of the observed transition and classification of its type, and naturally restricted the choice of microscopic models. Furthermore, it was confirmed that the transition may be treated as the result of oxygen atoms disordering over two sublattices: the anion lattice which is initially occupied by oxygen atoms, and the cation lattice with sites located in the centres of anion sublattice cubes so that the half of them is occupied by uranium atoms and another half is empty. As it follows from experimental data the cations are practically fixed in their sites up to the melting temperature, so that anion disordering over the two sublattices proceeds in the 'external' crystal field of the cations. The specific form of the free energy functional obtained in Refs. [8,9] is connected with the peculiarity of the space (O_h^5) group of crystals with the fluorite structure, which affords the conservation of the

space symmetry even after complete disordering of the anions over the two sublattices. As a result, this functional describes the transition which may be classified as a continuous phase transition in the external field and for this reason is accompanied by the onset of an anomaly in the specific heat smeared in some temperature range. The results of this analysis impose serious restrictions on the form of the entropy term in microscopic models and require a more detailed and self-consistent description of defect spatial distribution over the crystal lattice sites. This mainly concerns the description of blocking of the neighbour sites for similar defects, which should take into account the real configuration and symmetry of the fluorite crystal lattice.

Thus the problem which is stated in the present work consists of two parts: (1) calculation of the configurational entropy of the defect distribution over the fluorite crystal lattice taking into account blocking of the neighbour sites, which reflects the real (specific) symmetry of the UO_2 crystal, and (2) consistent description of the screened Coulomb interactions of charged defects within the framework of the Debye–Hückel mechanism taking into account interactions of these defects also with the electronic subsystem of the UO_2 semiconductor crystal.

The matter of the first problem was stated above in detail. With respect to the second problem it is necessary to give some additional comments. The idea of Ref. [3] about the spontaneous increase of the charged defects generation at some critical level of their concentration which induces a mutual screening of the charges and self-consistently suppresses the effective formation energy of the defects, is certainly correct. However, explicit calculations in the frame of this and the subsequent model [2] lead to significantly higher values of the resulting defect concentration than measured in the experiment. The analysis of the results of the model [2] shows that the reason for such high values of the spontaneous defect generation is mainly connected with relatively large defect charges ($Z = \pm 2$, for positively charged oxygen vacancies and negatively charged oxygen interstitials respectively). However, a more detailed consideration of the charge state of vacancies shows that the charge of these defects can be significantly changed with the temperature increase owing to their interactions with the electronic subsystem of the UO_2 semiconductor crystal.

Indeed, in accordance with microscopic calculations of Catlow [10] of the UO_2 electronic structure based on the shell model, the vacancies of the oxygen sublattice can trap electrons (and form F-centres), since their electronic level ε_a is situated in the middle of the energy gap (with the width of ≈ 2 eV) near the position of the Fermi-level of the perfect (non-defected) crystal. Any variation of the defect concentration influences the Fermi-level position that in its turn leads to the self-con-

sistent variation of the degree of the electronic subsystem excitation and hence of the ϵ_a level filling, i.e. variation of the vacancy charge. On the other hand, the correlation energy of the system determined by the Coulomb interactions between charged lattice defects which form the solid state ‘plasma’, essentially depends on their charge Z : $E_{\text{corr}} \propto (\sum_a Z_a^2 N_a)^{3/2}$. Therefore, partial reduction of the vacancy positive charge induced by electron trapping considerably influences the collective system behaviour and, as it will be shown further, finally leads to a significant increase of the critical defect concentration which induces the spontaneous phase transformation in the system. This implies that both electronic subsystem excitations and defect lattice disordering are self-consistently responsible for the phase transition mechanism.

Simultaneous solution of the two parts of the stated problem allows the development of a microscopic model which provides an adequate quantitative description of the structural phase transition in the UO_2 crystal in the vicinity of T_{crit} (practically without using any fitting parameters).

2. Description of the model

In order to describe the behaviour of the point defect system in the UO_2 crystal, the free energy is presented in the standard form of the lattice gas approximation

$$F = wN + F_{\text{DH}} - kTS. \quad (1)$$

The first term in Eq. (1) is the formation energy of the Frenkel defect pair ($N_i = N_v = N$). In accordance with microscopic calculations [4], at high temperatures defects in the fluorite-type crystals form complexes which can be represented as short-living clusters termed (3:1:2). Each cluster consists of one Frenkel pair and two relaxing atoms next to the interstitial sites of the anion sublattice (see Fig. 1). Relaxing atoms are displaced in the direction to the centre of the uranium-free cube of the oxygen sublattice at the distance of 0.25–0.5 of the diagonal length. Vacancies which are formed due to the atom relaxation also make some contribution to the total amount of forming defects measured by the neutron scattering method [4]. On the other hand, the displacement of the relaxing atoms is fixed with respect to the anion sublattice sites as well as to the position of the prime interstitial in the cluster (see Fig. 1). Thus they do not make any additional (with respect to the prime interstitials) contribution neither to the correlation energy (F_{DH}) nor to the configurational entropy. For this reason, the value N will be regarded further as the number of the ‘real’ Frenkel pairs, or in other words, the number of the clusters, which (as it follows from the model of the (3:1:2) cluster) is three times lower than the total number

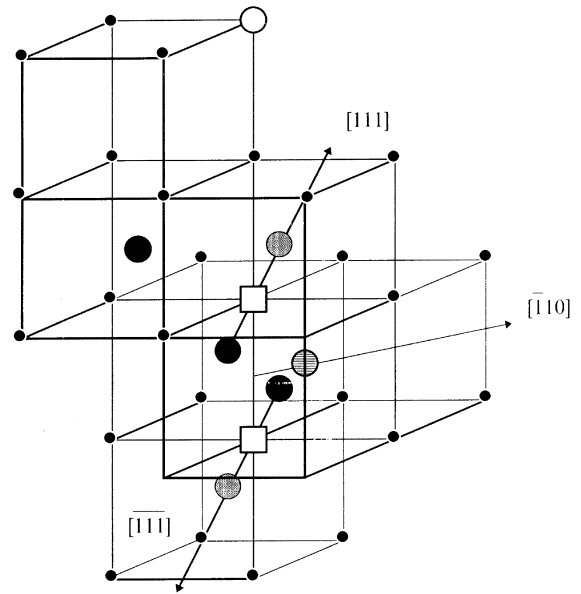


Fig. 1. Defect clusters (3:2:1) formed by the anion sublattice disordering at high temperature. (●) oxygen atoms (●) uranium atoms. Frenkel pairs: (⊙) interstitial, (○) vacancy, Relaxing defects: (⊙) interstitial (□) vacancy.

of interstitials (or vacancies) measured in the experiment.

The formation energy of an oxygen Frenkel pair is equal to 3.67 eV in accordance with the results [12] of the measurements of anion sublattice disordering at temperatures of about 2000 K. These measurements were carried out in the temperature range that was several hundred degrees below T_{crit} , i.e. far from the transition region, and hence the defect concentration was rather small $n \ll 0.01$. In this case calculating the equilibrium defect concentration according to Eq. (1) one can neglect the contribution of F_{DH} which is determined by the defect interactions. Hence the standard expression $n \propto \exp(-w/2kT)$ for the equilibrium concentration of Frenkel pairs can be used at these relatively low temperatures, which allowed the determination of the formation energy w of one pair. At higher temperatures in the vicinity of the phase transition the defect interactions F_{DH} cannot be neglected anymore, but the same value 3.67 eV for w must be used in the first term of Eq. (1).

The subsystem of point defects represents a lattice gas of charged particles, which interact with each other electrostatically. Thus in the mean-field approximation the correlation energy of their interactions takes the form ([11,13])

$$F_{\text{DH}} = - \frac{2\sqrt{\pi}e^3}{3e^{3/2}\sqrt{kTV}} \left(\sum_a N_a Z_a^2 \right)^{3/2}, \quad (2)$$

where e is the electron charge, T is the temperature, k is the Boltzmann constant, V is the volume, ε is the dielectric constant, N_a is the number of the particles of type a with charge Z_a . In the ordinary case the index $a = 1, 2$ denotes the positively charged vacancies ($Z_a = +2$) and negatively charged interstitials ($Z_a = -2$). In the considered case, as it will be shown further, the vacancies partially screened by the trapped electrons will also contribute to the general Eq. (2). In this model uranium Schottky vacancies are not taken into account due to their high formation energy 7–10 eV.

Calculations performed in Ref. [10] show that the vacancies and interstitials, which form Frenkel pairs in the anion sublattice of UO_2 , at low temperatures have the effective charges $Z = \pm 2$. These values were taken in Ref. [2] for the description of the high temperature transition, that led, however, to rather high values of correlation energy and too small defect concentrations with respect to the measured data (see Section 1). Calculations [10] of the crystal electronic spectrum also demonstrated that UO_2 is a semiconductor with the energy gap of ≈ 2 eV, this was repeatedly confirmed experimentally (see, for example, Ref. [14]). It was also shown, that oxygen vacancies form F-centres and are able to trap an electron on the free level of the F-centre. This level is situated approximately in the middle of the energy gap, that is near the position of the Fermi-level of the perfect (non-defected) crystal. An upper filled level of the interstitials O_i^{2-} lies below the valence band and thus does not take part in the excitation of the electronic system.

The existence of an electronic level of vacancies in the energy gap of semiconductors can lead to important consequences in the behaviour of a system of interacting defects and electrons, that was often discussed in the literature. As an example, one can adduce the phenomenon of so-called ‘self-compensation’ in doped semiconductors (see, for example, Ref. [15]). In order to increase the number of current carriers (for example, electrons in the conduction band), a semiconductor is doped with ambivalent admixtures. However, in certain cases instead of the transfer of admixture electrons to the conduction band, it is more preferable for the system to form vacancies with free electron levels and to trap the admixture electrons in these levels. As the result of this process, the number of carriers in the conduction band does not increase and hence the conductivity also does not increase. Similarly in our case the existence of the electronic level of anion vacancies in the middle of the energy gap can lead to a strong screening of these vacancies by the trapped electrons and hence to the decrease of their effective charge. Consideration of the interactions among the electrons and point defects can lead to a significant reinforcement of the electronic subsystem excitation.

At finite temperature T the electron distribution over energy levels ε_i obeys the Fermi–Dirac statistics.

$$f(\varepsilon_i) = \left(1 + \exp\left(\frac{\varepsilon_i - \mu}{kT}\right)\right)^{-1}. \quad (3)$$

The position of the Fermi level (chemical potential) μ is determined self-consistently by the electrical neutrality of the system

$$n_e + n_a = n_h, \quad (4)$$

where n_e is the electron concentration in the conduction band, n_a is the electron concentration at the F-centres, n_h is the hole concentration in the valence band; $n_a = n f(\varepsilon_a)$, n is the anion vacancy concentration. It is easy to show that in the considered case the exponential factors μ/kT and $(\varepsilon_g - \mu)/kT$ are large enough ($\mu \approx 1$ eV, $\varepsilon_g \approx 2$ eV, $kT \approx 0.25$ eV), so that one may use the standard relations for a non-degenerated semiconductor for the description of the occupation of the conduction band by electrons and of the valence band by holes [16]

$$\begin{aligned} n_e &= \frac{2}{m} \left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{\mu - \varepsilon_g}{kT}\right), n_h \\ &= \frac{2}{m} \left(\frac{m_h kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{\mu}{kT}\right), \end{aligned} \quad (5)$$

where $m_e \approx m_0$, $m_h \approx 10 m_0$ are the effective masses of electrons and holes (m_0 is the mass of a free electron), $m \approx 4.48 \times 10^{22} \text{ cm}^{-3}$ is the concentration of the anion sublattice sites, ε_g is the width of the energy gap.

From Eq. (5) it is seen, that the degree of the electronic subsystem excitation and hence the degree of the vacancy screening are determined by the Fermi level position. At low temperatures when the defect concentration is low, the solution of the system of Eqs. (3)–(5) yields an estimation for the value of the chemical potential $\mu \approx \varepsilon_g/2$, which results in

$$n_a \ll n_e \approx n_h \approx \exp\left(\frac{\varepsilon_g}{2kT}\right). \quad (6)$$

With temperature and the corresponding defect concentration increase the contribution of n_a to the balance, Eq. (4), also increases and in the vicinity of T_{crit} turns out to be the dominating one, so that the chemical potential decreases to the value $\mu \approx \varepsilon_a/2$. In this case, instead of Eq. (6) the following relationship takes place:

$$n_e \ll n_a \approx n_h \approx \exp\left(-\frac{\varepsilon_a}{2kT}\right). \quad (7)$$

This relation allows us to neglect n_e in Eq. (4) and to obtain from Eq. (5) the relation between n and n_h

$$n_h = \frac{2n}{1 + \left(1 + \frac{n \exp(\varepsilon_a/kT)}{2(kT)^{3/2}}\right)^{1/2}} \quad (8)$$

Substituting the values $n \approx 0.07$ and $kT \approx 0.3$ eV corresponding to the transition region, into Eq. (8) it is easy

to obtain a proximity $n_h \approx n$ which is consistent with Eq. (7).

Thus in the temperature region of the phase transition the lattice gas of charged particles comprises the following defects: oxygen interstitials with the charge $Z_i = -2$ and concentration $n_i = n$; completely ionised oxygen vacancies with $Z_v = +2$, $n_v = (1-f)n$; oxygen vacancies with occupied electronic level, $Z_a = +1$, $n_a = nf$; holes with $Z_h = +1$ and concentration n_h . Finally the sum in Eq. (2) takes the form

$$\sum_a N_a Z_a^2 = (8n - 2n_h) M, \quad (9)$$

where M is the number of the anion sublattice sites.

From Eq. (9) it is seen, that the interactions between the electronic and point defect subsystems lead to a significant decrease of the correlation energy (in comparison with the results [2]), since a new term $2n_h$ has the same order of magnitude as the term $8n$.

As pointed out in Ref. [17] it is also possible that the holes in the valence band are spatially localised and form small polarons U^{s+} . In this case Eq. (7) takes the form

$$n_h = \frac{2n}{1 + (1 + 8n \exp(\varepsilon_a/t))^{1/2}}. \quad (10)$$

Further this case will be regarded as well.

For the calculation of the entropy contribution to the free energy functional, Eq. (1), it should be taken into account that the Coulomb interaction which is screened at large distances, leads to a strong repulsion between identical defects at short (interatomic) distances. Thus following Ref. [2] for the calculation of the number of possible configuration states one should consider that the installation of one oxygen vacancy leads to the reduction of the number of remaining free sites for distribution of other vacancies by seven (one place is occupied by the defect itself and six places are blocked). When the vacancy concentration is sufficiently high, neighbour vacancies may block the same sites. This results in a decrease of the effective number of the sites which are blocked by one vacancy in comparison with the case of a dilute vacancy gas. In the Appendix A possible configurations of interacting defects in the fluorite type crystal are considered and on this basis the vacancy contribution to the configurational entropy is calculated.

The contribution of the interstitials O_i^{2-} to the entropy can be considered analogously. In the beginning it is assumed that the O_i^{2-} ions can be located in the identical positions inside uranium-free cubes of the oxygen sublattice (for example, in their centres). These positions form an fcc lattice with the lattice parameter equal to two interatomic distances in the oxygen sublattice. A test defect located in a site of this lattice (see Fig. 2) blocks 12 nearest neighbours – sites of type (1).

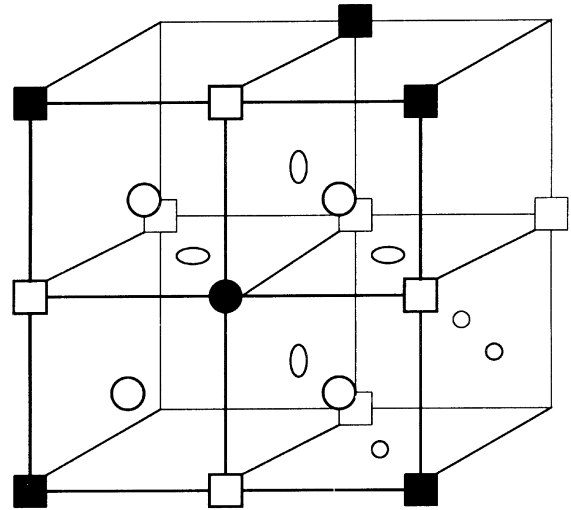


Fig. 2. Arrangement of different types of sites near a test defect in the sublattice formed by the interstitials: (●) test defect (○) blocked lattice sites (1) (□), (■) (○) sites (2), (3) and (4), capable of blocking sites (1).

For the determination of the mean number of sites blocked by a test defect it is necessary as in the previous case (see Appendix A) to consider all possible configurations of the interstitial distribution over the sites of types (2), (3), (4) and their probabilities. However, in this case the problem is more complicated since the distribution of the particles over these sites is not independent. Thus for the calculation of the number of states the following approximation will be used. In the case when the interstitial concentration is so high that all possible positions are occupied and all the nearest neighbours to the occupied positions are free as the result of blocking, defects will occupy sites of one of the four simple cubic sublattices which compose the origin fcc lattice. This configuration is considered as a new ground state (4-fold degenerated). The number of sites of each new sublattice is $K = M/8$, where M is the number of sites of the anion sublattice. If the number of interstitials N is less than K , then $(K-N)$ free sites are formed in the sublattice. As the result, the number of states which corresponds to the given number of interstitials will be equal to

$$C_K^{K-N} = C_K^N.$$

As follows from the calculations [4], in reality O_i^{2-} interstitials are not located in the centres of cubes of the anion sublattice but are shifted to one of their edges (see Fig. 1). Thus each interstitial can occupy one of 12 various positions inside the cube. Besides, relaxing atoms of the clusters (3:1:2) may be displaced in two different directions, so that the total number of states of a cluster which is located around a given sublattice site is

equal to 24. Finally, the total number of states which contribute to the configurational entropy of the interstitial subsystem is equal to

$$\Gamma = 24^N C_K^N.$$

The contribution to the configurational entropy determined by the interstitial distribution yields

$$S = n \ln 24 - n \ln n - (0.125 - n) \ln(0.125 - n). \quad (11)$$

In Ref. [6] the vibrational entropy of Frenkel pairs was calculated at high temperatures (above the Debye temperature)

$$\Delta S = -k \ln \left(\frac{\prod_i^{3N} \omega_i}{\prod_i^{3N} \omega_i} \right), \quad (12)$$

where ω_i is the spectrum of a perfect crystal, ω_i is the spectrum of a crystal with defects. The value $\Delta S \approx 4k$ obtained as the result of these calculations is the contribution of the non-configurational entropy to the general expression (1).

Substituting Eq. (2) into Eq. (1) with account of Eq. (9) and Eqs. (A.1), (11) and (12) which determine various entropy contributions, and using the above presented values of the numerical parameters, one finally obtains the specific value (per one site of the anion sublattice) of the free energy:

$$F = 3.67n - \frac{0.09(8n - 2n_h)^{3/2}}{\sqrt{kT}} + kT(2n \ln n + (0.125 - n) \ln(0.125 - n) S_i(n) - 7.1n), \quad (13)$$

where F and kT are expressed in electron volts (eV), the hole concentration n_h is defined by Eqs. (8) and (10).

It should be emphasised that usually (see, for example, Ref. [12]) the term in the free energy which is proportional to nkT is defined solely by the contribution of the non-configurational (e.g. vibrational) entropy. In the present model an additional term from the configurational entropy, Eq. (11) also contributes to this expression. As the result, the coefficient before nkT will be approximately equal to 7, that is in agreement with the results of the experiments [14] where this value was estimated from the specific heat measurements in the temperature range from 300 to 1500 K.

3. Results and discussion

For the description of the high temperature behaviour of uranium dioxide, namely for the determination of the degree of the anion sublattice disorder and temperature dependence of the specific heat, it is necessary to investigate the system of Eqs. (8) and (13). The equilibrium concentration of vacancies in the oxygen

sublattice is determined by minimisation of the free energy functional, Eq. (13) under the condition that the hole concentration is determined by Eq. (8). Currently, the position of the electronic level of the vacancy F-centre ($\varepsilon_a \approx$ eV) is a calculated value (Ref. [10]) and was not measured experimentally. For this reason, the dependence of the defect concentration on temperature was calculated by variation of ε_a in the vicinity of the above indicated value 1 eV. Calculated dependencies $N(T)$ are shown in Fig. 3 for three values of ε_a , and also available experimental data from Ref. [4] are presented for comparison. As indicated above, vacancies which are formed due to the atom relaxation in the cluster (3:2:1) also give some contribution (together with vacancies forming real Frenkel pairs) to the total amount $N(T)$ of the defects measured in the experiment. Accordingly, the value $N(T) = 3n(T)$ is represented in Fig. 3, where $n(T)$ corresponds to the minimum of the free energy functional $F(n)$ calculated from Eq. (13) for a given temperature T .

When ε_a increases, the transition region (that is the temperature range in which a significant change in the equilibrium defect concentration and a corresponding steep increase in the specific heat occur) displaces to lower temperatures and hence to smaller concentrations. This means that with the increase of ε_a the degree of the electron subsystem excitation decreases for the given temperature. Consequently the screening of vacancies by electrons also decreases, so that the value of the correlation energy for the given defect concentrations increases. For larger values of $\varepsilon_a (> 1.05$ eV) the hole concentration becomes extremely small in comparison with the vacancy concentration $n_h \ll n$, so that excitations of the electronic subsystem do not influence anymore the behaviour of the point defects. In fact this

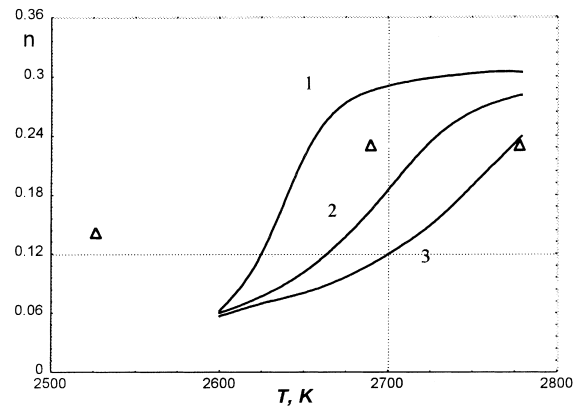


Fig. 3. The calculated temperature dependence of the equilibrium defect concentration for various values of ε_a : 1 – $\varepsilon_a = 1.05$ eV, 2 – $\varepsilon_a = 0.97$ eV, 3 – $\varepsilon_a = 0.9$ eV. Marker (Δ) denotes experimental data from Ref. [4].

particular case corresponds to the model [2] in which the electronic subsystem was not considered at all. Besides, for large values of ε_a the increase of the equilibrium vacancy concentration with temperature becomes rather steep, so that for $\varepsilon_a > 1.05$ eV in the vicinity of the phase transition the equilibrium concentration changes by jump, but not gradually. Such a behaviour is in contradiction with the results of general phenomenological considerations of this transition [8] and with experimental observation [4].

When ε_a decreases, the region of the transition shifts to higher temperature and the defect concentration growth becomes smoother. Correspondingly, the height of the specific heat peak decreases and its width increases. For these reasons, the value $\varepsilon_a \approx 0.97$ eV was chosen as one describing the characteristics of the considered transition in the best way, namely the type of the transition following from the phenomenological consideration, the transition temperature T_{crit} , the range of the defect concentration variation and the form of the excessive specific heat peak.

The specific heat calculations were carried out in accordance with the thermodynamic relation $C = -T(\partial^2 F/\partial T^2)$. The temperature derivatives were calculated after substitution of the equilibrium concentration $n(T)$ into the free energy functional. The value $\varepsilon_a \approx 0.97$ eV simultaneously provides the best fitting of the calculated curve $N(T)$ and the excessive specific heat peak form (the height of the peak $\delta C_{\text{max}} \approx 100$ J/K mol. and its width $\delta T \approx 80$ K) to the measured data [4] (see Fig. 4).

The calculation of the temperature dependence of the equilibrium vacancy concentration can be performed also for the case of the localised holes when their concentration is determined by Eq. (10). In this case a satisfactory quantitative agreement of a $N(T)$ dependence

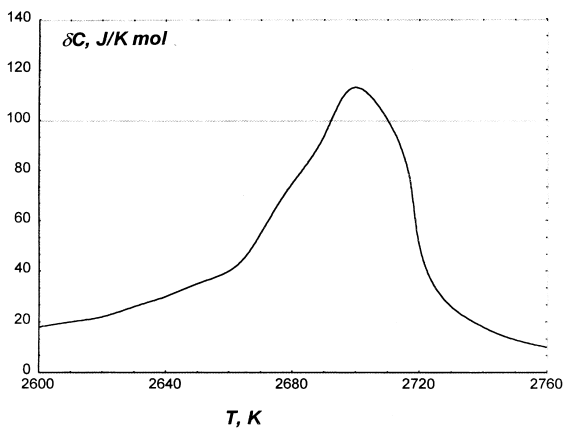


Fig. 4. Temperature dependence of the excess specific heat δC (J/K mol) for $\varepsilon_a = 0.97$ eV.

with measurements was attained for lower values $\varepsilon_a \approx 0.88$ eV, that is also in a good accordance with the theoretical value $\varepsilon_a \approx 1$ eV.

It should be mentioned that the value of the non-configurational entropy (which in the present model is determined by the coefficient before nkT in the free energy functional) is also approximate. For this reason, an assessment of the $N(T)$ behaviour for small variations of this value within the interval of $\pm 5\%$ was performed. The obtained variations in the concentration behaviour appeared to be negligible.

In connection with the above presented analysis some critical remarks concerning the configurational entropy calculations in some other models may be presented. For example, results of the configurational entropy calculations in Ref. [2] with account of neighbouring lattice sites blocking can be approximately represented in the form

$$S_{\text{conf}} = -2n \ln(n) + (0.5 - 13n) \ln(0.5 - 13n) + (1 - 7n) \ln(1 - 7n), \quad (14)$$

where the factors 13 and 7 determine the decrease of the number of vacant sites with installation of one defect in the interstitial and vacancy subsystems, respectively. The number of defects which can be distributed over the lattice sites must not exceed the total number of these sites. This directly corresponds to the positive sign of the logarithm arguments in Eq. (14) and consequently implies that the defect concentration n cannot exceed $1/2 \times 13 \approx 0.04$. Hence the behaviour of the system in the phase transition region with typical defect concentrations $n \approx 0.1$ cannot be described in the frames of this model at all.

An attempt to take into account simultaneous blocking of the same sites by several defects (so that the effective number of blocked sites decreases with the defect concentration increase) was made in Ref. [5]. The following expression for the configurational entropy was deduced: $\ln(C_N^{\alpha M} \cdot C_N^{2\beta M})$, where α and β are some functions of N ; in particular, $\alpha = (1 + 18(N/M))^{-1}$. A similar analysis to the previous case analysis of the model gives for the maximum possible defect concentrations $n = N/M$ the value of ≈ 0.11 , which is in a direct contradiction with the value $n \approx 0.2$, calculated by this model [5] for temperatures above the transition temperature T_{crit} .

4. Conclusions

A new model is proposed for the quantitative description of oxygen sublattice disordering and the anomalous specific heat behaviour of the uranium dioxide crystal in the vicinity of the high temperature

phase transition to the superionic state. This model is essentially based on the previous model proposed in Ref. [2] where the ionic nature of the UO_2 crystal with electrostatic interactions of charged defects was taken into consideration. In accordance with the model [2], self-consistent screening of the charged defects due to the Debye-Hückel mechanism strongly reduces the formation energy of the Frenkel pairs. At some critical defect concentration which can be attained at elevated temperatures this leads to the spontaneous generation of new defects and steep increase of their concentration. Since the electrostatic interaction of the defects at interatomic distances is not screened and is very large, blocking of neighbour sites by similar defects should be taken into account in the configurational entropy calculations. Consideration of these factors in Ref. [2] allowed a qualitative explanation of the phase transition mechanism, however, numerical calculations of the critical defect concentration by this model which determined the commence of the superionic transition was by two orders of magnitude lower than the value measured in Ref [4].

In the present model a satisfactory coincidence of the obtained results with experimental data was attained by consideration of the following two factors:

(i) An important parameter, which determines the value of the correlation energy in the system of electrostatically interacting defects is the charge of these defects. Point defects of the crystal lattice play a crucial role in the description of high-temperature phase transition in uranium dioxide. Usually the charges of these defects were taken to be equal to $Z = \pm 2$, for positively charged oxygen vacancies and negatively charged oxygen interstitials, respectively. However, a more detailed consideration shows that the charge state of the vacancies may significantly change with the temperature increase in the result of their interactions with the electronic subsystem of the UO_2 semiconductor crystal. In accordance with numerical calculations of the electronic structure of the UO_2 crystal [10], the oxygen vacancies form F-centres with the electronic level situated in the middle of the energy gap close to the Fermi-level of the perfect crystal. The increase of the defect concentration with temperature escalation influences the position of the Fermi-level, that in turn leads to a self-consistent variation of the ϵ_a level filling. This interplay radically influences the effective vacancy charge and hence the behaviour of the system in general. Thus, the new mechanism proposed in the present paper implies that both the electronic subsystem excitations and the defect lattice disordering are self-consistently responsible for the high-temperature transformation of the crystal. (ii) The strong Coulomb repulsion of similarly charged defects unscreened at small distances leads to blocking of the nearest sites. Consideration of this phenomenon results in the reduction of a number of

possible positions for the distribution of similar defects and hence the expression for the configurational entropy changes. General phenomenological considerations of the transition behaviour of the system performed in Refs. [8,9] impose strong restrictions on the form of the free energy functional and in particular on the form of the configurational entropy. This requires a more detailed and consistent description of the defect distribution over the crystalline lattice sites, especially, a more exact consideration of site blocking at small distances with account of the real symmetry of the fluoride crystal lattice.

The consideration of these two factors allowed the development of the microscopic model, which provided a quantitative description of the structural transition in the UO_2 crystal in the vicinity of T_{crit} , adequate to the experimental observations. In particular, a satisfactory coincidence was attained of numerical model calculations with the following measurements: (i) a significant increase of the anion sublattice disorder was observed with temperature escalation from 2650 to 2730 K, so that the equilibrium defect concentration in this temperature range increased from 0.02 to 0.25 (with respect to one site of the oxygen sublattice); (ii) correspondingly, the anomalous behaviour of the specific heat $C(T)$ was characterised by a wide peak with the maximum height $\delta C_{\text{max}} \approx 100 \text{ J/K mol}$ and the width of the temperature interval of smearing $\delta T \approx 80 \text{ K}$.

On the basis of the developed model, a critical consideration of the previously proposed models for the description of the superionic transition in UO_2 was carried out.

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Appendix A

In the Appendix A the mean number of lattice sites that are blocked by one vacancy is calculated in the case when the vacancy concentration differs from zero. A test defect is located in the lattice site (0) (Fig. 5) and blocks 6 neighbour sites (1) from the first co-ordinate sphere. The lattice site (1) could be already blocked if other defects are located in the sites of the types (2) and (3). The lattice sites (2) and (3) are not the nearest neighbours for each other, so the probability P of the defect position in each lattice site is independent and equal to n , where n is the mean defect concentration. The total number of the lattice sites (2) and (3), from which the site (1) can be blocked is equal to 18.

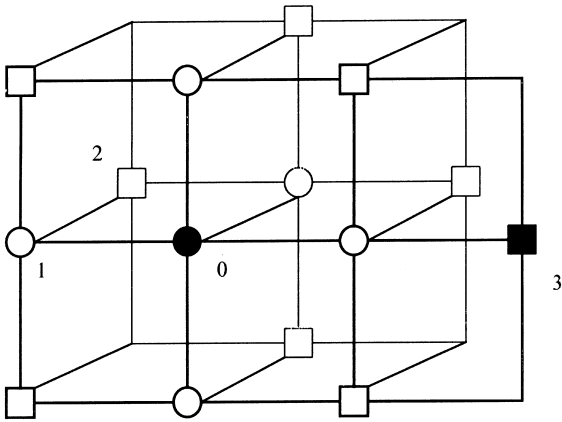


Fig. 5. Arrangement of various type sites near a test defect in the anion sublattice ● denotes the test defect (0); (○) blocked site (□) (■), site of types (2) and (3) of the second and third coordinate spheres, respectively.

The probability of the lattice sites (2) and (3) to be vacant is equal to

$$P_6 = (1 - n)^{18},$$

where index 6 indicates that the test defect blocks 6 lattice sites.

The probability for one lattice site (1) to be already blocked and that the test defect blocks 5 lattice sites (1) is equal to

$$P_5 = 6(1 - n)^{17}n.$$

The probability for two lattice sites to be already blocked is equal to

$$P_4 = 12 \times (1 - n)^{17}n + 15(1 - n)^{16}n^2 + 24(1 - n)^{16}n^2,$$

where the first term is the probability for one defect to be located in the lattice site (2), the second – for two defects to be located in the lattice site (3), the third – for two defects to occupy the nearest lattice sites of type (2) and (3), so that two lattice sites (1) are blocked. In the same way the following probabilities are calculated within the accuracy of n^2

$$P_3 = 48(1 - n)^{16}n^2 + 30(1 - n)^{16}n^2,$$

$$P_2 = 36(1 - n)^{16}n^2.$$

Ultimately for the mean number of lattice sites which are blocked by a test defect one obtains

$$\alpha(n) = \frac{\sum_{k=2}^6 kP_k(n)}{\sum_{k=2}^6 P_k(n)} = 6 - 30n - 867n^2.$$

On this basis the number of states Γ for the system of N defects which occupy M possible lattice sites, can be calculated. Similarly to the simple system when one particle occupies one lattice site, one can write

$$\Gamma = \frac{1}{N!} M \left(M - \left(1 + \alpha \left(\frac{1}{M} \right) \right) \right) \left(M - \left(2 + \alpha \left(\frac{1}{M} \right) + \alpha \left(\frac{2}{M} \right) \right) \right) \cdots \left(M - \left(N - 1 + \sum_1^{N-1} \alpha \left(\frac{k}{M} \right) \right) \right).$$

For $M \gg 1$ the sum in each factor can be replaced by an integral

$$\sum_{k=1}^k \left(1 + \alpha \left(\frac{k}{M} \right) \right) = M \int_0^{\frac{k}{M}} (1 + \alpha(x)) dx = M\beta \left(\frac{K}{m} \right) = M \left(7 \left(\frac{K}{M} \right) - 15 \left(\frac{K}{M} \right)^2 - 286 \left(\frac{K}{M} \right)^3 \right).$$

As a result the following expression for the entropy can be obtained

$$S_v = \ln \left(\prod_{k=0}^N \left(M - M\beta \left(\frac{K}{M} \right) \right) \right) - N \ln \left(\frac{N}{e} \right) = \sum_{k=0}^N \ln \left(1 - \beta \left(\frac{K}{M} \right) \right) - N \ln \left(\frac{N}{Me} \right).$$

Again replacing the sum by an integral, one obtains the final expression for the vacancy contribution to the configurational entropy

$$S_v = M \left\{ \int_0^n \ln (1 - 7n + 15n^2 + 286n^3) dn - n \ln n + n \right\}. \tag{A.1}$$

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