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Ionic conductivity in Gd-doped CeO₂: *Ab initio* color-diffusion nonequilibrium molecular dynamics study

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A first-principles nonequilibrium molecular dynamics (NEMD) study employing the color-diffusion algorithm has been conducted to obtain the bulk ionic conductivity and the diffusion constant of gadolinium-doped cerium oxide (GDC) in the 850–1150 K temperature range. Being a slow process, ionic diffusion in solids usually requires simulation times that are prohibitively long for *ab initio* equilibrium molecular dynamics. The use of the color-diffusion algorithm allowed us to substantially speed up the oxygen-ion diffusion. The key parameters of the method, such as field direction and strength as well as color-charge distribution, have been investigated and their optimized values for the considered system have been determined. The calculated ionic conductivity and diffusion constants are in good agreement with available experimental data.

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I. INTRODUCTION

Substantially high oxygen-ion conductivity in the 850–1150 K temperature range makes ceria a promising electrolyte material for intermediate temperature solid oxide fuel cells (SOFCs) [1]. For these applications ceria is often doped with rare-earth elements that increase the amount of oxygen vacancies leading to enhanced oxygen-ion conductivity [2,3]. For instance, doping perfect CeO₂ with Gd, whose valence is +3, leads to the formation of one vacancy (V_O^{••}) for each pair of Gd atoms according to the reaction

where the Kröger-Vink notation [4] is used.

Many experimental and theoretical studies of the oxygen-ion conductivity of Gd-doped ceria (GDC) have been conducted over the past years. In particular, Steele *et al.* [3] and Wang *et al.* [5] measured the total conductivity as a function of oxygen partial pressure and temperature employing a four-probe dc method [3] and a two-probe ac impedance method [5], respectively. Different theoretical approaches to the calculation of conductivity have also been applied. For instance, Andersson *et al.* assessed the effect of doping on the ionic conductivity of ceria by using static energy barriers calculated within the framework of density functional theory (DFT) [6], Dholabhai *et al.* used the kinetic Monte Carlo (KMC) method based on a limited set of diffusion rates calculated with DFT [7], and Burbano *et al.* performed molecular dynamics simulations with custom interatomic potentials [8]. However, the agreement among the results of different theoretical works and experiment is rather poor, indicating the need for a better theoretical description of oxygen diffusion in doped ceria.

One of the widely used theoretical approaches to calculate the ionic conductivity is to apply the Arrhenius equation together with static energy barriers obtained from DFT calculations at $T = 0$ K. In this case the effect of temperature on activation energy is accounted for via an exponential factor.

The effect of atomic vibrations is hidden in a prefactor, which is often set according to a typical vibrational frequency of the diffusing atoms [9]. Another way to calculate ionic conductivity based on the migration barriers obtained at 0 K and the Arrhenius equation is to use the KMC method [10,11]. This method is suitable for the simulations of rare events such as, in many cases, diffusion in solids. It allows for the collection of extensive statistics and can be used for very large systems and long simulation times. However, the method needs all the diffusion rates of the system as input, and the validity of the obtained results is limited by the accuracy of the rate estimation [9].

Equilibrium molecular dynamics (MD) based on the Newtonian equations of motion is a computational approach, which allows for the explicit modeling of diffusion at different temperatures. In classical MD, the interactions among atoms are described with empirical or semiempirical interatomic potentials. These potentials provide the possibility to run calculations at moderate computational cost for relatively large systems. The creation of accurate and transferable potentials is, however, a difficult task, especially for complex materials. In *ab initio* molecular dynamics (AIMD) the interactions between the atoms are calculated on-the-fly from the fundamental laws of quantum mechanics. The major disadvantage of this method is that the computational cost can be excessively high due to a large mismatch of the time scales of the atomic vibrations and the diffusive events. Therefore, collecting sufficient statistics within reasonable simulation time with AIMD becomes problematic [9].

The Born-Oppenheimer nonequilibrium molecular dynamics (NEMD) method based on the color-diffusion algorithm [12] speeds up diffusion, making it possible to study a system of vibrating atoms and to obtain much better statistics of diffusive jumps compared to equilibrium MD. This method has successfully been applied to study lithium ion conduction in LiBH₄ by Aeberhard *et al.* [13]. In this work we apply the NEMD approach combined with the color-charge technique to study the oxygen-ion conductivity in Gd-doped cerium oxide. We have carefully investigated the effect of the key parameters of this method, i.e., the magnitude and the direction of the color field, the color-charge distribution, and the choice

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of initial configuration on the oxygen-ion conductivity. The chosen optimal set of parameters has further been used to calculate the temperature dependencies of the conductivity and the diffusion coefficient of GDC.

The paper is organized as follows. In Sec. II, the general idea of the NEMD technique combined with the color-charge algorithm is discussed. The details of calculations and the description of the considered GDC structure used in this study are given in Sec. III. In Sec. IV the key parameters of the method and the temperature dependence of the oxygen-ion conductivity in GDC are discussed. Section V summarizes our work.

II. METHODOLOGY

The main idea of the color-diffusion algorithm is that in order to accelerate the diffusion in molecular dynamics one applies a fictitious color field, $\mathbf{F}_{\text{ext}}$, acting only on the diffusing atoms. To make these diffusing atoms feel the field one assigns them with the so-called color charges, c_i . The rest of the atoms remain color-charge neutral and, therefore, “blind” to the color field. As a result, the color field acting on the color-charged oxygen ions speeds up their diffusion while leaving the movement of other atoms nearly unperturbed. The action of the field is similar to that of an electric field in an ionic system. However, in contrast to the electric charges, there are no interactions between the color charges. The external field takes the system out of thermodynamic equilibrium, but the system can reach a steady state characterized by constant temperature and constant color flux. In principle, it is sufficient to consider only one type of color charges, e.g., $c_i = +1$, which are all accelerated along the direction of the field. This creates a nonzero net color charge in the system. In some cases in order to keep the system color-charge neutral, two types of color charges can be considered, namely $+1$ or -1 . The $+1$ charges tend to move along the field, while the -1 charges prefer to move in the opposite direction. In this case the net color charge in the system can be set to zero. However, if a nonzero net charge of the system does not influence the conductivity, it is convenient to use only one type of color charges, either positive or negative.

In the presence of the color field, an atom i will experience a force equal to $c_i \mathbf{F}_{\text{ext}}$ in addition to the usual force $\mathbf{F}_i$ obtained in standard equilibrium MD. That is, the Newtonian motion will be governed by

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + c_i \mathbf{F}_{\text{ext}} \quad \forall i \in \{\text{O}, \text{Ce}, \text{Gd}\}, \quad (2)$$

where $\mathbf{p}_i$ is the momentum of atom i . Notice that according to a standard AIMD procedure (implemented in the code used in our simulations, see below in Sec. IIIA) any net force, including the one resulting from the nonzero total color charge, is automatically removed at each time step of the simulation by subtracting a fraction m_i/m_{tot} of the total force from each atom, where m_i is the mass of atom i and m_{tot} is the total mass of the system.

The work produced by the artificial external field introduces extra heat into the system. This heat can be removed by applying a thermostat. To minimize the influence of the thermostat on the diffusion process, we apply it to the non-diffusing Ce and Gd ions only. The temperature of the

O ions is then controlled by their heat exchange with the Ce/Gd subsystem. We use a velocity scaling thermostat, which maintains the temperature by scaling the momenta according to

$$\mathbf{p}_i \rightarrow \sqrt{\frac{T_0}{T}} \mathbf{p}_i \quad \forall i \in \{\text{Gd}, \text{Ce}\}, \quad (3)$$

where T_0 and T are the desired and actual temperatures of the Ce/Gd subsystem, respectively. The velocity scaling thermostat is an approximate version of the Gaussian thermostat, with the error of order of the MD time step, Δt . Thus, with a reasonably small Δt , the results of both thermostats are very similar [14]. This legitimizes the use of the velocity scaling thermostat in the present simulations.

The application of the field changes the total momentum of the system. To shift the total momentum back to zero we shift the momentum of all the Ce and Gd ions according to

$$\mathbf{p}_i \rightarrow \mathbf{p}_i - \frac{1}{N_{\text{Ce/Gd}}} \sum_{j \in \{\text{Gd}, \text{Ce}, \text{O}\}} \mathbf{p}_j \quad \forall i \in \{\text{Gd}, \text{Ce}\}, \quad (4)$$

where $N_{\text{Ce/Gd}}$ is the number of atoms in the Ce/Gd subsystem.

The application of the color field takes the system out of the equilibrium state and the response of the system is a color flux in the direction of the field. The flux is defined as

$$J_c(t) = \frac{1}{V} \sum_{i=1}^N c_i v_i(t) \quad \forall i \in \{\text{O}\}, \quad (5)$$

which is analogous to an electric current density, where $v_i(t)$ is the projection of the velocity of atom i onto the direction of the field and V is the volume of the cell. After an initial transient period the system reaches a steady state with constant temperature and constant color flux. Linear-response theory in the steady state provides the connection between the color flux and the diffusion coefficient, D , of the color-charged atoms [12],

$$D = \frac{k_B T}{\rho_c} \lim_{t \rightarrow \infty} \lim_{F_{\text{ext}} \rightarrow 0} \frac{\langle J_c(t) \rangle}{F_{\text{ext}}}, \quad (6)$$

where $\rho_c = N_O/V$ is the density of color-charged particles defined as the number of oxygen atoms, N_O , over the volume of the cell. The angular brackets $\langle \dots \rangle$ denote averaging over time. From this relation the ionic conductivity of the system can be obtained via the generalized Nernst-Einstein equation [12]

$$\sigma = \frac{(Ze)^2 \rho_c}{k_B T} D, \quad (7)$$

where Ze is the charge of an oxygen-ion equal to -2 elementary charges. Then the final conductivity expression is

$$\sigma = (Ze)^2 \lim_{t \rightarrow \infty} \lim_{F_{\text{ext}} \rightarrow 0} \frac{\langle J_c(t) \rangle}{F_{\text{ext}}}. \quad (8)$$

The first limit, $t \rightarrow \infty$, requires statistics over infinitely long time in order to obtain the correct results, although, practically it means that one needs a long-enough MD run to ensure convergence. Concerning the second limit, one aims at restoring the properties of the system with no artificial field applied. At the same time, one wants to avoid calculations

for small fields at which the diffusion is hardly accelerated and the convergence over time becomes as slow as in standard equilibrium MD. However, one can safely use the fictitious color field to speed up the diffusion as long as the response of the system to the applied field, i.e., the color flux, is a linear function of the field. If one stays in the linear regime the ratio between the flux and the field is constant, i.e., it gives the same value of conductivity. Certainly, the higher field one chooses the more one accelerates the diffusion. Therefore, our goal is to find the highest possible value of the field, which still allows us to stay in the regime of predominantly linear flux response.

III. DETAILS OF CALCULATIONS

A. *Ab initio* nonequilibrium molecular dynamics setup

The Born-Oppenheimer NEMD simulations were performed using our implementation of the color-diffusion algorithm in the Vienna Ab Initio Simulation Package (VASP) [15–17], with the projector augmented wave (PAW) method [18] as the basis. Electronic exchange and correlation effects were modeled within the generalized gradient approximation (GGA) [19]. To get accurate atomic forces, convergence tests with respect to the plane-wave cutoff and k -points mesh density were carried out. As a result, the plane-wave cutoff of 400 eV and $1 \times 1 \times 1$ k -point mesh (i.e., Γ point) were chosen.

The equations of motion were integrated using the Verlet algorithm with the time step $\Delta t = 2$ fs. This time step was found to be suitable by performing calculations with a smaller time step of 1 fs. They showed no essential difference in the results. In order to collect the required statistics corresponding to sufficiently long time in the steady state with constant flux, the total simulation time was of about ~ 50 ps, i.e., 25 000 MD steps, for each run. Initial velocities were set randomly according to the Maxwell-Boltzmann distribution at a chosen temperature. The time needed to equilibrate the system was usually within ~ 1 ps (500 initial MD steps) of the simulations. To make sure that the equilibration period was sufficiently long, we performed an additional calculation at the initial temperature of 1000 K with a longer (15 ps) equilibration period. The resulting conductivity value (0.21 S cm^{-1}) is in excellent agreement with the one for the shorter equilibration period (0.19 S cm^{-1}).

B. Structure

The $2 \times 2 \times 2$ supercell of GDC used in this study consisted of eight fluorite unit cells with one oxygen atom removed and with two Ce atoms replaced by Gd atoms. The total number of atoms in the cell was 95, comprised of 30 Ce atoms, 2 Gd atoms, and 63 O atoms with the chemical formula $\text{Gd}_{0.0625}\text{Ce}_{0.9375}\text{O}_{2-\delta}$, where $\delta = 0.03125$ (see Fig. 1). Thus, the dopant concentration was 6.25 at. %. The configuration with the two dopants placed as a pair of nearest neighbors was considered. Several initial vacancy positions were chosen in the structure, as we aimed to collect different vacancy trajectories during the run (see Fig. 1, positions 1, 2, and 3). The calculated equilibrium lattice constant at temperature $T = 1000$ K, $a = 5.47 \text{ \AA}$, was used. The considered temperature range 850–1150 K was chosen for its practical relevance for various applications.

FIG. 1. The GDC supercell. Large blue circles are Gd atoms, light green circles are Ce atoms, and small red circles are O atoms. Hollow circles are the oxygen vacancies in the initial configurations 1–3. a is the lattice parameter. Note that the individual initial configurations have only one vacancy. The Gd-dopant concentration is 6.25 at. %.

IV. RESULTS

In order to check the applicability of the method to the system under consideration, we tested the validity range of its key parameters, i.e., the external color field magnitude and direction, the distribution of color charges, and the initial position of the oxygen vacancy with respect to the dopants. Their influence on the oxygen-ion conductivity of Gd-doped ceria was evaluated.

A. Color-charge distribution and type

To create charge configurations ensuring the absence of preferred directions of the vacancy migration, we tested two possible charge distributions. First, a homogeneous configuration with only positively charged oxygen ions ($c_i = +1$) creating a large net color charge of $+63$ in the oxygen sublattice (single color configuration), was chosen. In this configuration all the oxygen ions were pulled by the applied color field in the $[111]$ direction. The migration occurred via jumps in the $\langle 100 \rangle$ directions.

Second, in order to check the influence of the nonzero total color charge on the resulting conductivity we tested another configuration. This time the color charges were initially distributed among the oxygen atoms in a regular “3D checkerboard” pattern such that all neighboring atoms had opposite charges and the vacancy was initially surrounded by color charges of one sign. This distribution of charges was therefore also homogeneous in the $\langle 100 \rangle$ directions of the oxygen sublattice. The introduction of an oxygen vacancy into the system resulted in an uneven number of oxygen ions. Therefore, the number of positive and negative charges was different. We set the charge of 32 atoms to $+1$, and the charge of 31 atoms to -1 , which resulted in a net color charge $+1$ in the oxygen sublattice. To keep the total color charge in the system at zero we distributed the excess charge of -1 equally over the ions in the cation sublattice, resulting in a small color charge of 0.03125 on every cation.

Our calculations showed that the presence of considerable total color charge in the system (single color configuration) did not qualitatively influence the ionic conductivity compared to the color charge almost neutral system. Resulting conductivity values are essentially identical (see Fig. 5). Therefore, in the following calculations only the single color configuration was used.

B. Color field direction and value

In the fluorite structure of the Gd-doped cerium oxide the migration of vacancies occurs in the simple cubic oxygen sublattice in the $\langle 100 \rangle$ directions, as was mentioned above. It basically means that in the absence of an external field, it is equally likely that any of the six nearest-neighbor oxygen atoms will jump into the vacancy. However, the applied field stimulates the movement of charged oxygen ions along the field. Therefore, in the single color configuration, for three of the six oxygen atoms it becomes more favorable to occupy the particular vacancy, while the other three are pulled away from it by the field. In order to create a situation without directional preference for vacancy migration we chose to apply the color field in the $[111]$ direction. The field in the $[111]$ direction is the only one, which provides equal opportunities for the accelerated diffusion in all the $\langle 100 \rangle$ diffusion paths, i.e., the experimentally known main diffusion paths in the system. Therefore it allows for the most efficient and unbiased diffusion simulation.

As discussed above, the color field magnitude is chosen as large as possible in order to accelerate the diffusion. A larger number of registered diffusive jumps leads to better statistics, which is needed for an accurate calculation of the ionic conductivity. On the other hand, the field magnitude should be sufficiently small to keep the system within the predominantly linear-response regime. To obtain the proper value of the field we first calculated the color flux at different color field values to find the limit of the linear regime (see Fig. 2). As one can see from Fig. 2 the precision of the calculations is sufficient to judge that fields higher than $0.6 \text{ eV/\AA}$ lead to a strongly nonlinear response, while below

FIG. 2. The time-averaged response (color flux in the $[111]$ direction) vs the field strength (squares) calculated from Eq. (5). The dotted line represents the linear fit of the points up to $0.5 \text{ eV/\AA}$.

$0.5 \text{ eV/\AA}$ the response appears to be largely linear. Therefore, we used $0.5 \text{ eV/\AA}$ field value in all subsequent simulations.

C. Initial vacancy position

In this study we tested different initial vacancy positions relative to the Gd dopants in the considered GDC fluorite structure, with the color charges distributed in the single color configuration.

In order to make sure that proper statistics is gathered one needs to check that the steady state is reached during the simulation run, i.e., that the resulting flux in the direction of the field is constant in time. Unfortunately, there are certain positions in the cell whose occupation probabilities are influenced by the direction of the color field.

For instance, any configuration where the vacancy is situated in the first nearest-neighbor shell of the dopants corresponds to the lowest energy state of the system and therefore represents a natural trap for the vacancy. This is reflected in a somewhat longer time spent by the vacancy in such positions. However, in the nearest neighbor vacancy position an unphysical trapping can also occur. This happens when the oxygen ion is pulled towards the two Gd atoms by the field. The oxygen ion then has to take the path between the two dopants and therefore needs to overcome a large energy barrier [6]. This unphysical trapping of the vacancy due to the chosen field direction unavoidably influences the statistics of the jumps.

It is practically difficult to eliminate these contributions and obtain the proper time of the vacancy occupation in the case when both types of trapping are present. Therefore, we preferred to avoid this situation by choosing the initial positions of the vacancy away from the trapping position and monitored the vacancy trajectory during the whole run. That was the motivation for the three initial positions, numbered 1, 2, and 3 in Fig. 1, to be used in this work.

To improve the statistics one can combine the results from different trajectories at a given temperature, as it was done in this work. In subsequent calculations we averaged conductivities corresponding to the three chosen initial configurations for every considered temperature. As one can see from Table I, the actual temperatures obtained via the averaging of the system temperature over time with the initial temperature 1100 K were slightly different for different starting configurations

TABLE I. Conductivities at $T \sim 1146 \text{ K}$ calculated according to Eq. (8) for different initial vacancy positions are shown in comparison with the experimental data interpolated to the actual averaged temperature of the calculations. The simulation time in all the runs was about 50 ps . Numbers after “This work” in the right column label initial positions of the vacancy (see Fig. 1).

$T \text{ (K)}$	$\sigma \text{ (S cm}^{-1}\text{)}$	Origin
1147	19.4×10^{-2}	This work 1
1132	16.4×10^{-2}	This work 2
1159	22.3×10^{-2}	This work 3
1146	10.9×10^{-2}	Wang <i>et al.</i> [5]
1146	9.7×10^{-2}	Jud <i>et al.</i> [20]
1146	4.6×10^{-2}	Burbano <i>et al.</i> [8]

FIG. 3. Time-averaged conductivity vs time calculated according to Eq. (8). The final converged conductivity value is shown with black dashed line.

(1132–1159 K). For averaging, only the simulation runs where the system reached a steady state, with the flux constant over the time, were chosen.

Table I shows the calculated conductivities for the GDC system at temperatures around 1146 K for the three initial vacancy configurations 1–3. As one can see, the obtained conductivity values are rather close to each other: $\sim 16.4\text{--}22.3 \times 10^{-2}$ S/cm. The moderate distinction in the values originates from different vacancy trajectories in the cell. The vacancy-dopants distances govern the energetics of the configurations along the path and therefore lead to different times between diffusive jumps. This level of agreement indicates that the used simulation time (about 50 ps) is long enough for sufficient statistics to be gathered. The procedure of collecting conductivity data from different trajectories and averaging them over the different runs allows for more accurate estimation of the ionic conductivity.

The final conductivity value, which can be compared to the experimental values (Fig. 5), is obtained by averaging the conductivities from different runs at the temperature, which in turn was obtained by averaging the actual temperatures of individual runs. In Table I the experimental [5,20] and previous theoretical [8] values of the ionic conductivity in the GDC system with 10 at. % of Gd interpolated to the considered averaged temperature of $T = 1146$ K are shown for comparison. The experimental values ($\sim 9.7\text{--}10.9 \times 10^{-2}$ S/cm) are of the same order of magnitude as those calculated in this work. A more detailed analysis can be found in Sec. IV E.

D. Statistics and efficiency

By monitoring the conductivity σ and flux $\langle J \rangle$ as functions of time, we found that they converged to a constant value after about 20 ps of simulation time. An example of conductivity convergence is given in Fig. 3. The convergence is similar for most of the initial configurations and temperatures, ensuring that the simulations were sufficiently long for calculating the conductivity.

Figure 4 shows a typical example of the mean-square displacement (MSD) at ~ 1146 K of the oxygen ions calculated for one of the initial configurations with the considered single color-charge distribution. The vertical steps on the MSD

FIG. 4. Mean-square displacement of oxygen atoms vs time. The steps indicate diffusive jumps.

curve indicate the diffusive jumps, whose number can be roughly estimated to 55. As one can see from Fig. 4, the time between the jumps can vary, but the MSD curve is smooth, demonstrating that a steady state was reached and therefore the flux is rather constant in time. An estimation of the time between the jumps can be done. Considering 55 jumps in ~ 42 ps gives us an average time between the jumps ~ 0.76 ps.

E. Temperature dependence of conductivity

We studied the temperature dependence of the conductivity of Gd-doped cerium oxide. The calculations were performed at four initial temperatures, with the single color-charge distribution and an external field of 0.5 eV/Å in the [111] direction. The actual averaged temperatures were 848, 934, 1038, and 1146 K. Figure 5 shows the simulated conductivities in comparison with the available experimental and theoretical data. The agreement between the obtained NEMD results and the experiment is rather good. As one can see, our results are slightly above the experimental curves. There are numerical and physical reasons for that.

The main numerical reason is a slight deviation of the response to the applied color field [13]. Due to the higher values of the color field the nonlinear effects shift the resulting conductivities toward higher values but allow one to substantially reduce simulation times. For example, our calculations showed that decreasing the field to 0.4 eV/Å means one has to spend at least three times more computational time to obtain the same number of jumps. The use of field 0.5 eV/Å allowed us to optimize the simulation times while staying in the predominantly linear regime and, therefore, to obtain a good estimate of conductivity and diffusion coefficient.

Further, as a matter of fact one should expect the theoretical conductivities to be larger than the experimental ones as in calculations we considered an ideal bulk monocrystalline material. Therefore, theoretical calculations done for bulk describe the grain conductivity rather than total conductivity, which consists of contributions of both grains and grain boundaries. The grain boundary contribution is expected to be smaller than the grain counterpart up to ~ 1000 K [23]. Experimental conditions always imply the presence of different 1D (e.g., dislocations) and 2D (e.g., grain boundaries) defects, which substantially reduces the conductivity. In particular,

FIG. 5. The oxygen-ion conductivity vs temperature calculated according to Eq. (8) for GDC. Our calculated oxygen-ion conductivities are shown with star symbols for the only positive color-charges distribution. For the comparison the calculated conductivity point for the 3D checkerboard distribution is shown with large red open circle. Open symbols represent the experimental data from Steele [3], Wang *et al.* [5], Jud *et al.* [20], Zhu *et al.* [21], and Zhou *et al.* [22]. All the experimental data are for 10 at. % of Gd. Theoretical data from the literature are shown with filled diamonds for classical potential MD, Burbano *et al.* [8], and with filled triangles for kinetic Monte Carlo simulations, Dholabhai *et al.* [7] (solid and dashed lines correspond to 10 and 5 at. % of Gd, respectively).

in the paper by Lin *et al.* [24] the authors show how a lower ionic conductivity at grain boundaries as compared to that of the grains leads to the decrease of the total ionic conductivity of Gd-doped ceria. Therefore, for an idealized model, considered in this as well as in previous theoretical works [8], the calculated conductivity should correspond to, at least, the upper limit for the experimental results. As one can learn from Fig. 5, that is only the case for the results of the present study.

According to our simulations the conductivity at temperatures up to 1000 K increases following the experimental trend. Starting from temperatures around 1000 K the obtained conductivity slope becomes more flat in contrast to the experimental curves. This difference may be a consequence of the electronic conductivity contribution, which is experimentally known to arise at high temperatures, or it could be connected to the fact that at high temperatures the grain conductivity becomes lower than the grain boundary conductivity [23]. Nevertheless, for all the considered temperatures the agreement with the experimental values is good and the slope of the conductivity curve mostly agrees with the experimental ones.

The diffusion coefficient was calculated at temperature $T = 1146$ K using Eq. (6). The obtained coefficient $D = 6.2 \times 10^{-7}$ cm²/s is in good agreement with the experimental value of $\sim 1 \times 10^{-7}$ cm²/s [25].

An important advantage of the NEMD approach compared with the traditional equilibrium MD technique is its computational efficiency. It is possible to estimate the frequency ν , for vacancy jumping for a certain temperature T , for instance, using the harmonic approximation [26]. There the transition rate of a vacancy moving from one site to another is given by $q = \nu \times \exp(-E_a/k_B T)$, where ν is the effective attempt frequency. It is often estimated as $\nu = 5 \times 10^{12}$ Hz

[26]. The attempt frequency obtained from experiment is of the same order, $\nu = 3 \times 10^{12}$ Hz [27]. E_a is the activation energy, which can be roughly estimated as ~ 0.5 eV from Ref. [6]. Accordingly, at $T = 1000$ K one diffusive jump should be expected every 60 ps. In our calculations, as it was mentioned above, the rough estimation gives one diffusive jump every 0.8 ps. This means that the achieved acceleration is about 60 times faster compared with the normal diffusion rate. This is a substantial advantage, meaning that the NEMD calculations require at least ~ 60 times less computational time than the equilibrium MD simulations. We directly checked the performance of equilibrium MD simulation by running it for 45 ps at 1000 K and, as expected, no diffusive jumps were registered.

V. CONCLUSIONS

Our calculations showed that NEMD combined with the color-diffusion algorithm is perfectly suitable for studying oxygen diffusion in systems like gadolinium-doped ceria. According to our estimations, the application of the NEMD methodology allowed us to speed up the simulated diffusion a factor 60 compared to standard equilibrium MD. The calculated conductivity values agree with the available experiment ones, and the experimental temperature trend is well reproduced. Our calculations showed that the results are sensitive to the choice of the key parameters, such as the external field direction and value, distribution of the color charges, and the simulation time. As a consequence it is important to properly test these parameters for every studied system. For Gd-doped cerium oxide, for example, it was important to set the field in the [111] direction and choose a homogeneous initial distribution of the color charges in

order to create a situation with no preferable directions for the vacancy diffusion.

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