

Calculation of native defect energies in α -Al₂O₃ and α -Cr₂O₃ using a modified Matsui potential

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Abstract

Alumina and chromia are very important materials in the surface coatings industry, e.g. for corrosion protection and as catalyst supports. The type of defects and the associated formation energy in these materials are of direct relevance to the surface stability and reaction kinetics. In the present work, a modified Matsui potential is applied to calculate the native point defect energies in α -Al₂O₃ and α -Cr₂O₃ based on the Mott–Littleton theory. Particular attention is paid to the convergence of the defect energies with the number of atoms surrounding the defect. The results show that the relative values of the defect formation energies are such that the Schottky energy is smaller than either of the Frenkel energies, which is in agreement with experimental data and recent results of first-principles calculations. The implications of these findings for diffusion mechanisms and the associated reaction kinetics are discussed briefly.

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1. Introduction

Alumina and chromia are very important materials in the surface coatings industry, e.g. for corrosion protection, catalyst supports, dielectric insulators, etc. The type of defects and the associated formation energy in these materials are of great importance for atomic transport and mechanical properties, and are of direct relevance to the surface stability and reaction kinetics.

Within the constraints of charge neutrality and stoichiometry, only two types of native point defects are allowed in α -Al₂O₃ and α -Cr₂O₃, i.e. Schottky and Frenkel defects. There are numerous theoretical studies on these intrinsic point defects in the corundum-type crystals, e.g. Al₂O₃ (Refs. [1–4]), Cr₂O₃ (Refs. [4–6]) and Fe₂O₃ (Refs. [4,5,7]). Most of these studies employed the same empirical shell model [8] (albeit with different parameter sets) combined with the Mott–Littleton approximation [9], although Catlow et al. [2,5] and Lawrence [6] also carried out calculations with an interatomic potential from a modified form of the electron-gas approximation. Very recently,

first-principles calculations have been performed for intrinsic defects in α -Al₂O₃ [10]. However, there is still some controversy over the dominant defect type in α -Al₂O₃. Some calculations [2,3] indicate that oxygen Frenkel defects have a lower formation energy than Schottky defects, while others [1,2,4,10] come to the opposite conclusion. As pointed out by Catlow et al. [2], this may in part be due to the difference in potential parameters used for describing the properties of α -Al₂O₃. As mentioned above, to date the Mott–Littleton approximation has been the predominant method to carry out calculations of defect energies. In contrast to first-principles calculations, the main advantages of the Mott–Littleton method are its easy implementation and low computational cost. In general, it is thought that approximately 100 atoms around a defect are sufficient for a convergence of the Mott–Littleton calculations [2]. However, about 40 atoms or less were also used to calculate defect energies [1,4]. Hence, it is necessary to examine the convergence of the results when the Mott–Littleton method is used.

In a previous paper [11] we developed a very simple potential from the model put forward by Matsui [12], which can describe the structure and lattice energy of α -Al₂O₃ very well. This “modified” Matsui model is very similar to shell models, except that in the latter a point charge is separated into a shell and a core. The shell is attached to the core by a spring and the overlap of

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shells results in a short-range repulsion. This modification leads to several additional parameters in the interaction potential, which requires at least the same number of experimental observables for their parameterisation [13]. In the present paper we will transfer this modified Matsui potential from $\alpha\text{-Al}_2\text{O}_3$ to $\alpha\text{-Cr}_2\text{O}_3$ in order to calculate the native point defect energies for both crystals. The convergence of the calculations using the Mott–Littleton approximation will be tested, the predicted order of native defect energies in stoichiometric $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ presented, and the importance of the investigated lattice defects for reaction kinetics and diffusion mechanisms etc. discussed.

2. Simulation details

In Ref. [11] we have modified the pair-interatomic potential proposed by Matsui [12] (where O = oxygen ion and M = metal ion) as follows

$$V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} - \frac{C_{OO}}{r_{ij}^6} + A_{OO} \exp\left(-\frac{r_{ij}}{\rho_{OO}}\right) + A_{MO} \exp\left(-\frac{r_{ij}}{\rho_{MO}}\right) \quad (1)$$

The potential parameters for $\alpha\text{-Al}_2\text{O}_3$ are taken from Ref. [11] and directly transferred to $\alpha\text{-Cr}_2\text{O}_3$. As in Ref. [14] we choose the van der Waals coefficient $C_{OO} = 32.32 \text{ eV } \text{\AA}^6$. The potential parameters for the Cr–O interaction are obtained with the computer programme GULP [15] via a fitting procedure described in Ref. [11]. The potential parameters for both $\alpha\text{-alumina}$ and $\alpha\text{-chromia}$ are summarized in Table 1. The calculated structural values for $\alpha\text{-chromia}$ ($a = 4.9872 \text{ \AA}$ and $c = 13.5582 \text{ \AA}$) are in excellent agreement with the observations ($a = 4.9570 \text{ \AA}$ and $c = 13.5923 \text{ \AA}$ [4]).

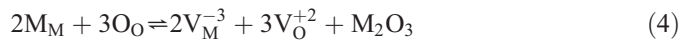
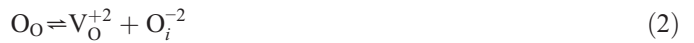
Following optimisation of the bulk crystal structures, the defect energies are calculated based on the Mott–Littleton approximation [9]. In a revised version of this method, the crystal surrounding a defect is divided into three spherical regions known as I, IIa and IIb [15]. Within region I the interactions are treated exactly at an atomistic level and all ions are explicitly allowed to relax to zero force in response to the defect. Region II extends from the edge of region I to a sufficiently large spherical surface. The inner region of which, IIa, acts as a transition between regions I and II. Interactions with ions in region IIa are calculated by a direct summation, but interactions with the outermost part, region IIb, are limited to a charge-induced dipole interaction involving solely the defect. The size of region I has to be large enough to ensure a convergence of the calculations. The defect energies were calculated using the computer code GULP [15].

Table 1
Potential parameters for $\alpha\text{-Al}_2\text{O}_3$ (from Ref. [11]) and $\alpha\text{-Cr}_2\text{O}_3$

	$\alpha\text{-Al}_2\text{O}_3$	$\alpha\text{-Cr}_2\text{O}_3$
A_{MO} (eV)	3411.118	2362.905
ρ_{MO} (Å)	0.244549	0.270628
A_{OO} (eV)	91.55955	91.55955
ρ_{OO} (Å)	0.547148	0.547148
q_O (e)	–2	–2
q_M (e)	3	3

3. Results and discussion

The crystals we consider here exhibit the corundum structure (space group $R\bar{3}c$) in which cations occupy the 12c sites and oxygen ions the 18e sites [16]. A cation vacancy is created by removing a metal ion from a 12c site to infinity, while an oxygen vacancy is created by removing an oxygen ion from an 18e site to infinity. The position between alternate pairs of cations (site 6b) was chosen as an interstitial site. The octahedral interstitial site has two cation nearest neighbours and six oxygen next-nearest neighbours. The vacancy formation energy is that required to create a vacancy and allowing the remaining lattice to relax to equilibrium. Likewise, the interstitial formation energy is that involved in bringing an ion from infinity to an interstitial site with a corresponding relaxation of the surrounding lattice [2]. Through combinations of the vacancy and/or interstitial formation energies, we can arrive at Frenkel pair and Schottky quintet energies ($2E_{OF}$, $2E_{MF}$ and $5E_{Sch}$), which are required for the following intrinsic defect reactions



where the subscript M denotes cations. We can also obtain the energy associated with interstitial disorder as defined in Ref. [2], which is required for the following reaction to take place



For a stoichiometric material, the Schottky and Frenkel energies are independent of the chemical potentials of O and Al [10].

3.1. Convergence test

Catlow et al. [2] noted that the convergence of calculations for noncubic systems is not as good as for cubic systems. Using the Mott–Littleton approximation, they also observed that the variation of the defect energy with the size of the inner region I may be nonmonotonic. Consequently, they suggested that, where absolute energies are important, large sizes of region I of the model should be used to ensure that satisfactory convergence is achieved. We have carried out similar convergence tests with the potential given in Eq. (1). The obtained results are shown in Fig. 1. As can be seen, when the region I contains less than about 200 ions, the variation of the defect energies E_{I_O} and E_{V_Al} , is nonmonotonic with increasing number of ions. Ultimately, however, the calculated energies decrease monotonically and gradually converge. The nonmonotonic behaviour is associated with the crystal structure of $\alpha\text{-Al}_2\text{O}_3$, i.e. when the radius of region I increases, the ratio of oxygen to aluminium in this region varies around the stoichiometric ratio which causes the small fluctuations of the defect energies. Hence, in order to obtain accurate absolute defect energy values for $\alpha\text{-Al}_2\text{O}_3$, less than 100 ions in region I are not enough, and more than about 500 ions are required for a convergence of

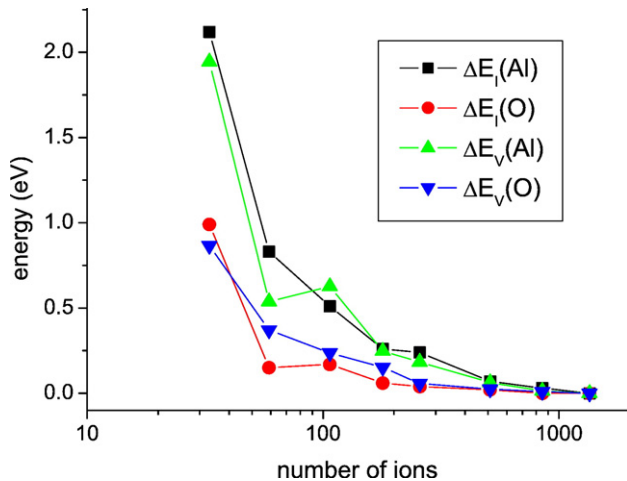


Fig. 1. Convergence of interstitial and vacancy energies in α - Al_2O_3 with increasing number of ions in region I (Mott–Littleton approximation). All energies are expressed as a difference with respect to the system with the largest region I. The lines are to guide the eye only.

≈ 0.1 eV. Although the Mott–Littleton approximation can still give reasonable estimates of point defect formation energies for small regions I (such as E_{IAl} , E_{IO} , E_{VAl} , and E_{VO}) we will see later that the values of E_{Sch} , E_{OF} and E_{AIF} are more sensitive to the size of region I.

3.2. Defect energies

The calculated defect energies for α - Al_2O_3 are summarized in Table 2. In this table, Catlow I and II refer to the empirical and nonempirical potential calculations of Catlow et al. [2]; Dienes represents the results of the shell model calculations of Dienes et al. [1], and Bush refers to results calculated by us with the dipolar shell model of Bush et al. [14]. The calculations of Catlow et al. [2] (Dienes et al. [1]) used 80 (30) ions in region I. As can be seen from this table, the present calculations agree best with the model put forward by Bush et al. [14] (see also discussion below).

Table 2
Defect energies and lattice energy (eV) for α - Al_2O_3

Defect	This work	Catlow I	Catlow II	Dienes et al. [1]	Bush et al. [14] ^a
O interstitial	−4.94	−16.59	−5.22	−10.1	−7.66
Al interstitial	−50.08	−43.87	−46.98	−34.4	−48.85
O vacancy	17.90	24.17	21.75	24.1	18.20
Al vacancy	60.17	54.30	61.15	54.3	57.15
Lattice energy	160.69	160.21	161.85	152.0	157.6
Schottky quintet	13.35	20.90	25.70	28.5	11.31
O Frenkel	12.96	7.78	16.54	14.0	10.54
Al Frenkel	10.07	10.44	14.18	20.0	8.30
Interstitial disorder	46.71	22.70	52.23	57.6	36.92

Catlow I and Catlow II correspond to empirical and nonempirical potential calculations [2], respectively.

^a Calculated here using the shell model of Bush et al. [14].

Table 3 shows the calculated defect energies (normalised per defect) for Frenkel pairs and the Schottky quintet in α - Al_2O_3 and α - Cr_2O_3 . Referring to this table, we find the following sequence of defect formation energies in α -alumina: $E_{\text{Sch}} < E_{\text{AIF}} < E_{\text{OF}}$. Our calculations are in reasonably good quantitative agreement with experiment [17] and the first-principles plane-wave pseudopotential calculations of Matsunaga et al. [10]. They are also in qualitative agreement with the nonempirical shell model calculations of Catlow et al. [2] and the model put forward by Bush et al. [14]. In contrast, the empirical calculations of Catlow et al. [2] and Lagerlöf et al. [3] predict $E_{\text{OF}} < E_{\text{Sch}} < E_{\text{AIF}}$, while Dienes et al. [1] and Atkinson et al. [4] suggest $E_{\text{Sch}} < E_{\text{OF}} < E_{\text{AIF}}$. We note, however, that the conclusion that Schottky defects are dominant in stoichiometric α - Al_2O_3 is also consistent with Mohapatra and Kröger's experimental results [17]. As can be seen from Table 3, the defect energy values obtained by first-principles calculations [10] are very close to the experimental values. It can also be seen that with the present, relatively simple model we arrive at values for E_{OF} and E_{AIF} which are in very good agreement with first-principles calculations [10], although our value of E_{Sch} is over 1 eV lower. However, there is a considerable disparity between our defect formation energies and, e.g. the values obtained by Catlow et al. [2], Dienes et al. [1] or Atkinson et al. [4]. This discrepancy may, in part, be due to the different number of ions in region I, however it mainly arises from the different potential parameter sets employed in the literature. It is also important to note that empirical interatomic potentials, which are usually obtained for perfect crystals, may not reflect accurately the distortion of the electron densities due to the introduction of a defect [10].

We now turn to the calculated point defect energies for α - Cr_2O_3 , which are also summarised in Table 3. As can be seen, the order of the defect formation energies for α - Cr_2O_3 predicted by the present model is the same as for α - Al_2O_3 , namely $E_{\text{Sch}} < E_{\text{CrF}} < E_{\text{OF}}$. This finding is in agreement with the simulations of Catlow et al. [5] and the empirical model of Lawrence et al. [6]. Lawrence et al. also

Table 3
Schottky quintet and Frenkel pair formation energies per defect (eV) for α - Al_2O_3 and α - Cr_2O_3

	Schottky	M Frenkel	O Frenkel	Reference
α - Al_2O_3				
Matsui (empirical)	2.67	5.03	6.48	This work
<i>Ab initio</i>	4.01	4.95	6.52	[10]
Experiment	3.83	4.45	—	[17]
Shell model	5.7	10.0	7.0	[1]
Shell (empirical)	4.18	5.22	3.79	[2]
Shell (nonempirical)	5.14	7.09	8.27	[2]
Shell model	5.17	6.59	4.87	[3]
Shell model	5.15	7.22	5.54	[4]
Shell model	2.26	4.15	5.27	[14] ^a
α - Cr_2O_3				
Matsui (empirical)	2.25	4.23	6.03	This work
Shell model	4.21	6.18	6.35	[5]
Shell (empirical)	4.03	6.15	7.09	[6]
Shell (nonempirical)	4.15	6.65	2.92	[6]
Shell model	5.59	7.80	5.34	[4]

^a Calculated here using the shell model of Bush et al. [14].

employed a nonempirical potential, however this model predicts a very low oxygen Frenkel pair formation energy. Atkinson et al. [4], using an empirical model with modified oxygen–oxygen potential parameters, arrived at quite different values for the defect energies, but obtained the same order as Lawrence et al. [6] with the non-empirical potential model, i.e. $E_{\text{OF}} < E_{\text{Sch}} < E_{\text{CrF}}$. In comparison with the results of Catlow et al. [5], Lawrence et al. [6] and Atkinson et al. [4], our value of the Schottky quintet energy is very low. However, in Ref. [4] (Ref. [5]) the region I contains only about 40 (120) ions, while in our calculations it contains over 1100 ions. We have repeated the calculations with a smaller radius of region I (to contain about 40 ions) and the calculated energies are $E_{\text{Sch}} = 3.70$ eV, $E_{\text{CrF}} = 6.44$ eV and $E_{\text{OF}} = 6.78$ eV, i.e. similar to the results obtained previously [4,5]. Finally, we note that we have also considered the possibility of defect association [10] where we have found a stabilisation of Frenkel pairs.

4. Conclusions

Using a modified Matsui potential and the Mott–Littleton approximation we have calculated the formation energies of point defects in $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$. The convergence of the calculated point defect energies was examined as a function of the system size. It was found that more than approximately 500 ions in region I are required for a convergence of the calculated vacancy and interstitial energies. The defect energy sequence of $E_{\text{Sch}} < E_{\text{MF}} < E_{\text{OF}}$, obtained by the present model for both $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$, is consistent with recent first-principles calculations. As was pointed out previously [4], Schottky quintets seem to be the dominant intrinsic point defects in $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$. Consequently, the metal cations are believed to be the more mobile species and are expected to diffuse via a vacancy mechanism. However, since the intrinsic defect energies in $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ are relatively large, the point defect chemistry in these materials will be controlled by small concentrations of aliovalent impurities [3]. Hence, cation vacancy compensation will dominate after tetravalent ions enter as cation substitutionals [2]. Recent advances in computing technology have enabled *ab initio* calculations of the stability and diffusion of oxygen vacancies in $\alpha\text{-Al}_2\text{O}_3$ [18,19]. Energy barriers for O-vacancy diffusion were found to be correlated to the Madelung potential at the saddle point for ionic compounds

and the stability of oxygen divacancies was demonstrated. These computing advances now also permit the study of very large systems (e.g. dislocations, grain boundaries, etc.) via pair-potential approaches such as the one put forward in the present paper.

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