DFT and QMC Studies of the Thermodynamics of Point Defects in Alumina QMC in the Apuan Alps IV

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Monday 28th July 2008

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Point Defects in Alumina

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Outline

Introduction

2 Alumina

3 Thermodynamics of Point Defects

4 Calculations and Results

5 Conclusions

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Outline



- Why Defects in Oxides?
- Opportunities for Electronic Structure Theory

2 Alumina

- 3 Thermodynamics of Point Defects
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Why Defects in Oxides?

AI_2O_3



Ti/Fe doped

Cr doped

Same mineral, different defects.











Opportunities for Electronic Structure Theory

- Most existing electronic structure studies of defects in oxides are bad. (There is some good work on semiconductors.)
 - Published DFT formation energies of neutral oxygen vacancy in alumina:
 - 12.92 eV, 10.14 eV, 5.83 eV, 7.08 eV, 13.3 eV.
 - Charged defects are even harder!
- Most existing electronic structure studies have not considered the thermodynamics of defect formation/migration.
- As Zhang and Northrup showed, combining DFT or QMC with thermodynamics gives a wealth of interesting and experimentally relevant data from a few accurate numbers.
- Plenty of opportunity for electronic structure theory and QMC to make a real impact on materials science.

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Outline





Alumina

- Physical Properties
- Crystal Structure
- Density of States and Bonding
- Point Defects
- Transport
- Some Questions



Calculations and Results

Conclusions

Alumina

Alumina is:

- Very hard (abrasive).
- Dense.
- Source of Al metal.
- Stable at high temperature (refractory).
- Used in lasers/optics.







Alumina Conical Crucible, 20ml, 1.299"TD x 0.906"BD x 4.4"H , 2/pack by Graphtek

No customer reviews yet. Be the first, | More about this product

Price: \$49.54

Availability: In stock. Processing takes an additional 4 to 5 days for orders from this seller. Ships from and sold by GraphiteStore

Product Features

are your own customer image: Composition: 99.8% Alumina

See larger image

- Maximum temperature: up to 3272 F (both oxidizing and reducing atmospheres)
- Density: 0.141lbs per cubic inch
- Porosity: 0%
- · Hard, chemically resistant, has the ability to withstand very high temperatures in aggressive environments

Product Description

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99.8% Alumina Conical Crucible, 20 ml capacity, Inert to hydrogen, carbon and refractory metals; can be used at operating temperatures to 1950 C in both oxidizing and reducing atmospheres.

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Alumina

Alumina is:

- Very hard (abrasive).
- Dense.
- Source of Al metal.
- Stable at high temperature (refractory).
- Used in lasers/optics.
- Easy! (No transition) metals or rare earths.)





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Structure of Al₂O₃

Complicated because of 2:3 coordination.



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Start with HCP lattice of O atoms



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Start with HCP lattice of O atoms



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Start with HCP lattice of O atoms



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Now add Al atoms



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Now add Al atoms



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Now add Al atoms



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Crystal Structure

... but remove one in three



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... and relax



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Density of States



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Bonding

The bonding is

- Mainly ionic
 - Clear from bandstructure.
 - ▶ Born effective charges close to +3 and -2.
- But has some covalent character
 - Point-charge and shell-model force fields do not work.

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Point Defect Types



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Neutral O Vacancy

Perfect crystal



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Neutral O Vacancy

Remove neutral O atom, electrons remain behind \Rightarrow V_O



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- The two electrons from the O²⁻ ion remain on the vacancy site, trapped in localised states in the band gap.
- The crystal remains locally neutral, so it's a neutral defect.

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Localised orbital on neutral oxygen vacancy



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Remove neutral O atom plus one localised electron \Rightarrow V₀⁺



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Remove neutral O atom plus two localised electrons \Rightarrow V₀²⁺



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• V₀⁺

- One localised electron remains on vacancy site.
- Crystal has local charge +1.
- V₀²⁺
 - No localised electrons remain on vacancy site.
 - Crystal has local charge +2.

Neutral Al Vacancy



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Neutral Al Vacancy

Remove neutral AI atom, holes remain behind \Rightarrow V_{A1}



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Neutral Al Vacancy

Or, more realistically ...



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- Charged Al vacancies V_{Al}^{-} , V_{Al}^{2-} and V_{Al}^{3-} are obtained by occupying the localised hole states.
- A similar notation is used for interstitials.
 - Al_I: Neutral Al atom on interstitial site.
 - Al_{I}^{+} : Al^{+} ion on interstitial site.
 - O_I^{2-} : O^{2-} ion on interstitial site

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In all cases, the charge assigned to the defect is the *change* in local charge when the defect is formed.

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Transport

Oxygen Transport

- High T properties depend on oxygen transport.
- Typical defect concentrations 1–10ppm.
- Cation substitutional impurities such as Mg²⁺, Ti⁴⁺, Ca²⁺ affect oxygen vacancy concentration dramatically.
- Identity of dominant diffusing species unknown.
 - Proposal of defect complexes such as V_{AIO}.

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Experimental Difficulties





Old data on lattice diffusion of O in Al₂O₃

New data on lattice diffusion of O in Al₂O₃



Lattice diffusion in Mgand Ti-doped AI_2O_3

Transport

Aluminium Transport

- Half-life of ^{26}Al is $\approx 7.2\times 10^5$ years!
- Measurements even more unreliable.

The Bottom Line

Intrinsic defects in alumina are not well understood

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Some Questions

- Are intrinsic defect concentrations always negligible?
- How sensitive are native defect concentrations to aliovalent impurity concentrations?
- How do the formation energies of native defects depend on doping?
- Why does the bulk diffusion data depend so little on doping?
- The corundum conundrum
 - ► Accepted theoretical estimate of formation energy of V₀²⁺ is ≤ 1 eV.
 - Activation energy for diffusion (sum of formation energy and barrier height) in "undoped" Al₂O₃ is about 6 eV from experiment.
 - Hence barrier height \approx 5eV. Far too high!

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- Equilibrium state minimises total Gibbs free energy

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- Work at constant T, P, N_{Al} , N_O .
- Equilibrium state minimises total Gibbs free energy

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- ► *N_i* is number of formula units containing defects of type *i*. (Perfect formula unit included.)
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- Assumes dilute limit.
- Assumes every defect fits into a formula unit.

Configurational Entropy

$$S_{\text{config}} = k_B \ln \frac{N! \prod_i m_i^{N_i}}{\prod_i N_i!}$$

- *N* is total number of formula units.
- *m_i* is multiplicity of sites and orientations of point defect *i* in a formula unit.

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$$G = \sum_{i} N_{i}g_{i} - TS_{\text{config}}$$

subject to

•
$$\sum_{i} N_{i} f_{i}^{\text{Al}} = N_{\text{Al}}$$

• $\sum_{i} N_{i} = N$

•
$$\sum_{i} N_{i} f_{i}^{O} = N_{O}$$

• $\sum_{i} N_{i} q_{i} = 0$

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$$G = \sum_{i} N_{i}g_{i} - TS_{\text{config}}$$

subject to

• $\sum_{i} N_{i} f_{i}^{AI} = N_{AI}$ • $\sum_{i} N_{i} f_{i}^{O} = N_{O}$ • $\sum_{i} N_{i} q_{i} = 0$

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•
$$\sum_i N_i q_i = Q_{imp}$$

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$$G = \sum_{i} N_i g_i - TS_{\rm config}$$

subject to

•
$$\sum_{i} N_{i} f_{i}^{AI} = N_{AI}$$

• $\sum_{i} N_{i} f_{i}^{O} = N_{O}$
• $\sum_{i} N_{i} q_{i} = Q_{imp}$

yields ...

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The Law of Mass Action

$$c_i = m_i \exp\left(-\frac{g_i - \mu_{AI}f_i^{AI} - \mu_O f_i^O + \mu_e q_i}{k_B T}\right)$$

- *c_i* is the concentration of defects of type *i*.
- The μ's are Lagrange multipliers for the atom-number and charge constraints.
- Sign of μ_e chosen to allow us to interpret it as a chemical potential for electrons.
- Since density of perfect formula units is almost 1,

$$g_{\mathrm{Al_2O_3}} pprox 2\mu_{\mathrm{Al}} + 3\mu_{\mathrm{O}}$$

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The Defect Formation Energy

• The law of mass action says that $c_i = m_i \exp(-\Delta g_i/k_B T)$, where

$$\Delta g_i = g_i - \mu_{\mathrm{Al}} f_i^{\mathrm{Al}} - \mu_{\mathrm{O}} f_i^{\mathrm{O}} + \mu_{e} q_i$$

is called the defect formation energy.

• Since
$$g_{
m Al_2O_3} pprox 2\mu_{
m Al} + 3\mu_{
m O}$$
, we obtain

$$\begin{aligned} \Delta g_i &= g_i - g_{\mathrm{Al}_2\mathrm{O}_3} - \mu_{\mathrm{Al}}(f_i^{\mathrm{Al}} - 2) - \mu_{\mathrm{O}}(f_i^{\mathrm{O}} - 3) + \mu_e q_i \\ &= g_i - g_{\mathrm{Al}_2\mathrm{O}_3} - \mu_{\mathrm{Al}}\Delta n_{\mathrm{Al}} - \mu_{\mathrm{O}}\Delta n_{\mathrm{O}} - \mu_e \Delta n_e \end{aligned}$$

where Δn_X is the number of particles (atoms/electrons) of type *X* added to the formula unit to make a defect of type *i*.

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Outline



2) Alumina



Calculations and Results

- The Grand Canonical Ensemble
- What Do We Need?
- Difficulties
- Formation Energies
- Defect Concentrations
- Transport

Conclusions

The Grand Canonical Ensemble

Although the Law of Mass Action was derived in the canonical ensemble, we now change viewpoints and treat μ_{O} and μ_{Al} as *inputs*.

 Imagine that the solid is in equilibrium with O₂ gas at (partial) pressure P_{O2} and temperature T

$$\mu_{\rm O} = \mu_{\frac{1}{2}{\rm O}_2}(P_{{\rm O}_2}, T)$$

- $\mu_{\rm Al}$ is then determined using $g_{\rm Al_2O_3} \approx 2\mu_{\rm Al} + 3\mu_{\rm O}$.
- $g_{Al_2O_3}$ will be calculated.

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- Choose $\mu_{\frac{1}{2}O_2}$ (and thus μ_O and μ_{Al}).
- Choose μ_e .
- Calculate defect formation energies

$$\Delta g_i = g_i - g_{\mathrm{Al}_2\mathrm{O}_3} - \mu_{\mathrm{Al}}\Delta n_{\mathrm{Al}} - \mu_{\mathrm{O}}\Delta n_{\mathrm{O}} - \mu_e\Delta n_e$$

Obtain defect concentrations from mass action equations

$$c_i = m_i \exp\left(-\frac{\Delta g_i}{k_B T}\right)$$

• Adjust μ_e until *Q* cancels the chosen impurity charge Q_{imp} .

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$$\Delta g_i = g_i - g_{\mathrm{Al}_2\mathrm{O}_3} - \mu_{\mathrm{Al}}\Delta n_{\mathrm{Al}} - \mu_{\mathrm{O}}\Delta n_{\mathrm{O}} - \mu_e\Delta n_e$$

Obtain defect concentrations from mass action equations

$$c_i = m_i \exp\left(-\frac{\Delta g_i}{k_B T}\right)$$

• Adjust μ_e until *Q* cancels the chosen impurity charge Q_{imp} .

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What Do We Need?

- The chemical potential of O_2 as a function of T and P_{O_2} .
- 2 The Gibbs energies per formula unit: g_i and $g_{Al_2O_3}$.

The Oxygen Chemical Potential

$$\mu_{\mathrm{O}_2} = (U + PV - TS)/N = E_{\mathrm{O}_2} + Pv - Ts$$

- The volume *v* and entropy *s* per molecule can be estimated using ideal gas formulae.
- With a good (multi-determinant) QMC calculation, the total energy E_{O_2} of an oxygen molecule could be obtained accurately enough to be useful.

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- With a good (multi-determinant) QMC calculation, the total energy $E_{\Omega_{2}}$ of an oxygen molecule could be obtained accurately enough to be useful.
- But not in DFT ...



The Finnis-Lozovoi-Alavi Method

• Consider formation of alumina from O₂ gas and Al metal at STP:

$$\Delta g^0_{
m Al_2O_3} = \mu^0_{
m Al_2O_3} - 3\mu^0_{rac{1}{2}O_2} - 2\mu^0_{
m Al}$$

- Given $\Delta g^0_{Al_2O_3}$ from thermodynamic tables, $\mu^0_{Al_2O_3}$ and μ^0_{Al} from calculations, obtain $\mu^0_{\frac{1}{2}O_2}$.
- Pressure and temperature dependence of μ⁰_{1/2O2}(P, T) from ideal gas law.

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Gibbs Energies of Solids

- For solids, PV and TS contributions to G are negligible (?).
- Hence $g_i \approx E_i$.
- Use DFT or QMC total energy calculations.

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Ingredients







Aluminium metal: $E_T[Al(s)]$





Alumina perfect crystal: E_T[Al₂O₃(s)]

etc ...

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Methods



Plane Wave DFT — CASTEP



Linear Scaling DFT — ONETEP



Diffusion Monte Carlo — CASINO

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Point Defects in Alumina

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- Plane-wave DFT calculations
 - CASTEP
 - Vanderbilt USP cut-off 550 eV; TN-DF cut-off 3000 eV.
 - LDA and GGA.
- DMC calculations
 - CASINO
 - DFT geometries.
 - Determinant from plane-wave calculation using TN-DF pseudopotentials.
 - Only Jastrow factor optimised (mostly VM).
- Cells and supercells
 - ► 1 × 1 × 1 hexagonal unit cell contains 30 atoms and 144 valence electrons.
 - The 2 × 2 × 1 simulation cell used for the DMC simulations contains 120 atoms and 576 valence electrons.
 - ▶ $3 \times 3 \times 2$ DFT supercell contains 540 atoms and 2592 electrons.

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Bulk Alumina in DMC

DFT geometry and lattice parameter work well:



Energy Gap much closer to experiment than DFT:

Method	Excitation Gap (eV)			
LDA-USP	6.9			
DMC	9.4(3)			
Experiment	9.1			

Difficulties

 Localised states in gap ⇒ self-interaction and band-gap problems in DFT.

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Difficulties

 Localised states in gap ⇒ self-interaction and band-gap problems in DFT. (But not in QMC, so skip these!)

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Difficulties

- Localised states in gap ⇒ self-interaction and band-gap problems in DFT. (But not in QMC, so skip these!)
- Charged defects \Rightarrow enormous finite-size errors.
 - Common correction is Makov-Payne

$$\Delta E_{MP} = -\frac{\alpha q^2}{2\epsilon L} + \mathcal{O}[L^{-3}]$$

- ► Hard to know what value of *e* to use and sometimes makes things worse.
- If approximation of pointlike defect charge is bad, MP-corrected results converge less quickly than uncorrected results.

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Makov-Payne Corrections

- Even when MP does not work, $E^{\text{def}}(1/L)$ is close to linear.
- Suggests using
 e as a fitting parameter rather than using experimental value.

$$\Delta E^{\rm def} = \frac{\alpha q^2}{2\epsilon L} + O[L^{-3}]$$

- Not enough points obtainable by scaling *L* in all directions system size becomes too large even after one doubling (120 atoms at 2 × 2 × 1, 960 atoms at 4 × 4 × 2)
- However, "real" variable is $v_M = \alpha/L$ with α shape dependent. For long, thin cells, v_M can even be negative.

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Extrapolation and Interpolation to Infinite Size

Calculate Madelung constants for various cell shapes. Choose cells giving a good spread of values of v_M .

Can *interpolate* to infinite size: safer than extrapolating.

Fitting ϵ to $E_{def}(v_M)$ works much better than using experimental ϵ . $\epsilon^{exp} \simeq 9.1, \epsilon^{fit} \simeq 3.57$



Extrapolation and Interpolation to Infinite Size

Method reliable for range of defects in alumina.

May not work so well with delocalised charges e.g. in semiconductors.



Formation Energies

Previous DMC calculations of defects have suggested that DFT may be overbinding the solid

Phys. Rev. Lett. **83**, 2351 (1999) Leung, Needs, Rajagopal, Itoh, Ihara. Calculations of Silicon Self-Interstitial Defects Phys. Rev. B **74**, 121102 (2006) Batista, ..., Martin, Umrigar et al Comparison of screened hybrid density functional theory to diffusion Monte Carlo in calculations of total energies of silicon phases and defects Interstitial formation energies 1-1.5eV higher in DMC than DFT.

Phys. Rev. Lett. **91**, 076403 (2003) Hood, Kent, Needs, Briddon Quantum Monte Carlo Study of the Optical and Diffusive Properties of the Vacancy Defect in Diamond Vacancy formation energy 1eV lower in DMC than DFT.

Bonds cost too much to break/form in DFT

⇒ Vacancy formation energies overestimated, Interstitial formation energies underestimated.

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DMC Formation Energies

$$\Delta g_i = g_i - g_{\mathrm{Al}_2\mathrm{O}_3} - \mu_{\mathrm{Al}}\Delta n_{\mathrm{Al}} - \mu_{\mathrm{O}}\Delta n_{\mathrm{O}} - \mu_{e}\Delta n_{e}$$



With bandgap correction, DFT appears to be significantly overbinding. Real cost to break bonds is lower.

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Point Defects in Alumina

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DMC Formation Energies

$$\Delta g_i = g_i - g_{\mathrm{Al}_2\mathrm{O}_3} - \mu_{\mathrm{Al}}\Delta n_{\mathrm{Al}} - \mu_{\mathrm{O}}\Delta n_{\mathrm{O}} - \mu_{e}\Delta n_{e}$$



Interstitial is consistently harder to form, also suggesting DFT overbinds.

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Point Defects in Alumina

Defect Concentrations



Questions

- Are *intrinsic* defect concentrations always negligible?
- How sensitive are native defect concentrations to aliovalent impurity concentrations?
- How do the formation energies of native defects depend on doping?



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Remember the Corundum Conundrum

Defect formation energies previously thought to be small (0.5–1eV). Activation energies of "undoped" Al_2O_3 known to be all \simeq 6eV from diffusion expts. Meant migration barriers must be $\simeq 5 \text{eV}$ — too high.

also

Identity of main diffusing species unknown. Effects of doping not well understood.

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Preliminary Answers

- Formation energies are *much* larger than previously thought closer to 5eV. Migration barrier need only be \sim 1 eV.
- $\bullet\,$ Main diffusing species is $V_{\rm O}^{2+}$ or $V_{\rm Al}^{3-},$ depending on sign of dopant charge.

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DFT Migration Barriers

Migration barriers to site-to-site diffusion of O vacancy.

Different paths show very different barriers (perhaps indicating strongly anisotropic diffusion).

Lowest barriers $\sim 1 \text{eV}$



DFT Migration Barriers

Migration barriers to site-to-site diffusion of Al vacancy.

Reveals unexpected configuration of notably lower energy.

Split vacancy along *c*-axis.



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Conundrum Resolved?

Combining migration barries \sim 1eV with vacancy formation energies for undoped Al₂O₃ gives:

$Q_{\rm O}^{\rm act}$	$Q_{\rm Al}^{\rm act}$
6.36	7.97

$$T = 1750K, P_{O_2}/P^0 = 0.1$$

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Effects of Doping on Activation Energy for Diffusion

 $Q_{\rm act} =$ formation energy + migration barrier

	Ti ⁴⁺		Mg ²⁺	
Dopant conc.	Q _O ^{act}	Q _{Al}	Q _O act	Q _{Al}
1ppm	8.28	3.98	3.41	8.97
5ppm	8.28	3.73	3.17	8.97
10ppm	8.28	3.63	3.07	8.97
100ppm	8.28	3.28	2.96	8.97
500ppm	8.28	3.04	2.96	8.97

Effect of doping with aliovalent impurities (Ti⁴⁺ and Mg²⁺) at T =1750K, $P_{\Omega_2}/P^0 = 0.2$.

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Outline

1 Introduction

2 Alumina

3 Thermodynamics of Point Defects

4 Calculations and Results

5 Conclusions

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Conclusions

- Defects in insulators interest materials scientists and technologists.
- Existing electronic structure work is of mixed quality.
- Quantum thermodynamics is quite fun!
- Run into limits of DFT.
- Lots of results from a few accurate calculations ⇒ opportunities for QMC.

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