

# Point Defects and Diffusion in $\alpha\text{-Al}_2\text{O}_3$

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- 1 Why?
- 2 Alumina and the Corundum Conundrum
- 3 Thermodynamics of Point Defects
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$\text{Al}_2\text{O}_3$



Ti/Fe doped



Cr doped

Same mineral, different defects.

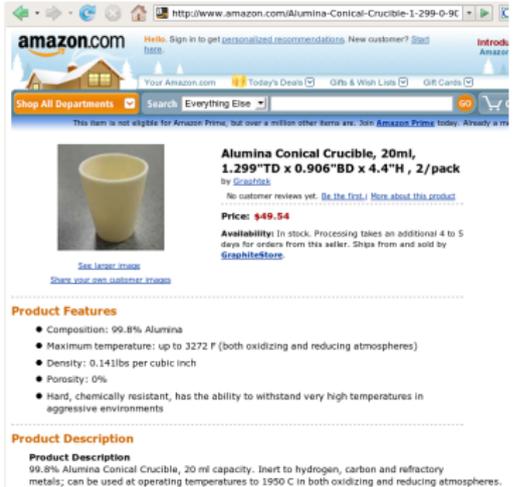
Alumina is the “prototypical” high-temperature ceramic.  
Properties depend strongly on defects and their diffusion coefficients.

- Electrical conductivity
- Grain growth
- Plastic deformation
- Oxide film growth
- Sintering and creep

The screenshot shows an Amazon.com product page for an Alumina Conical Crucible. The browser address bar shows the URL: <http://www.amazon.com/Alumina-Conical-Crucible-1-299-0-9C>. The page header includes the Amazon logo, navigation links like 'Hello, Sign in to get personalized recommendations', and a search bar with 'Everything Else' entered. Below the header, there is a promotional banner: 'This item is not eligible for Amazon Prime, but over a million other items are. See Amazon Prime today. Already a member? Sign in.' The product image shows a white, conical ceramic crucible. The product title is 'Alumina Conical Crucible, 20ml, 1.299"TD x 0.906"BD x 4.4"H, 2/pack by [GraghiteStore](#)'. The price is listed as '\$49.54'. The availability section states: 'Availability: In stock. Processing takes an additional 4 to 5 days for orders from this seller. Ships from and sold by [GraghiteStore](#).' The 'Product Features' section lists: 'Composition: 99.8% Alumina', 'Maximum temperature: up to 3272 F (both oxidizing and reducing atmospheres)', 'Density: 0.141lbs per cubic inch', 'Porosity: 0%', and 'Hard, chemically resistant, has the ability to withstand very high temperatures in aggressive environments'. The 'Product Description' section states: '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.'

Alumina is the “prototypical” high-temperature ceramic.  
Properties depend strongly on defects and their diffusion coefficients.

- Electrical conductivity
- Grain growth
- Plastic deformation
- Oxide film growth
- Sintering and creep
- No transition metals or rare earths!



The screenshot shows an Amazon.com product page for an Alumina Conical Crucible. The page includes a navigation bar with the Amazon logo, a search bar, and various utility links. The product title is "Alumina Conical Crucible, 20ml, 1.299\" TD x 0.906\" BD x 4.4\" H, 2/pack by [Graftech](#)". The price is listed as \$49.54. The availability section states "In stock. Processing takes an additional 4 to 5 days for orders from this seller. Ships from and sold by [GraftechStore](#)".

**Product Features**

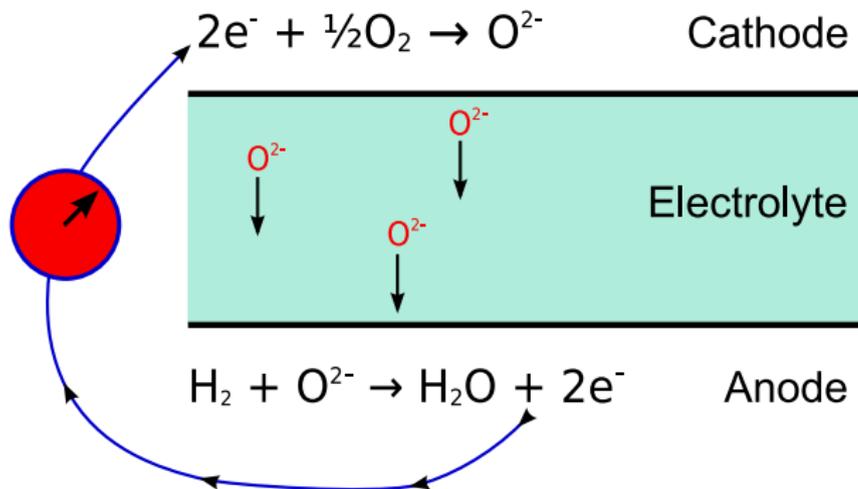
- Composition: 99.8% Alumina
- Maximum temperature: up to 3272 F (both oxidizing and reducing atmospheres)
- Density: 0.141lbs per cubic inch
- Porosity: 0%
- Hard, chemically resistant, has the ability to withstand very high temperatures in aggressive environments

**Product Description**

**Product Description**  
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.

- Classical force fields often inadequate.
- Much existing QM work on defects in oxides is bad. (There is good work on defects in 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!
- Few existing QM studies have considered the thermodynamics of defect formation/migration.
- Model for many other problems of technological and scientific interest.

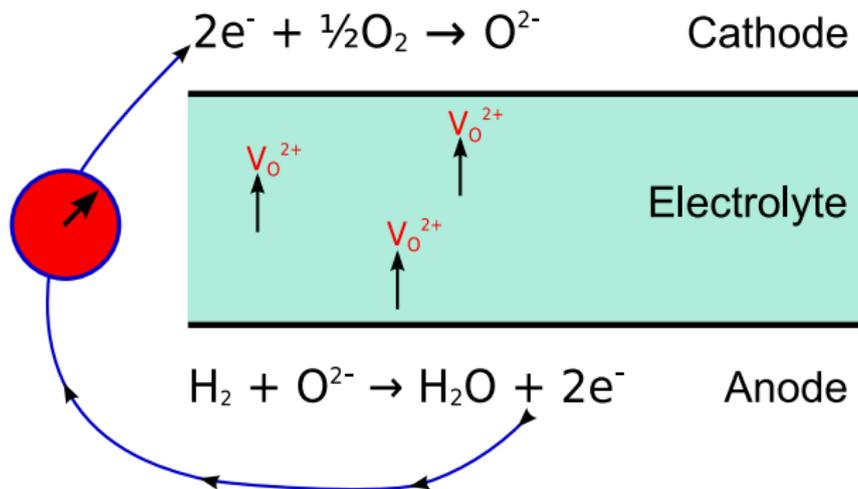
## Solid Oxide Fuel Cells



- Electrolyte must conduct ions but not electrons.
- $ZrO_2$  (open structure).
- $CeO_2$  (variable valence):



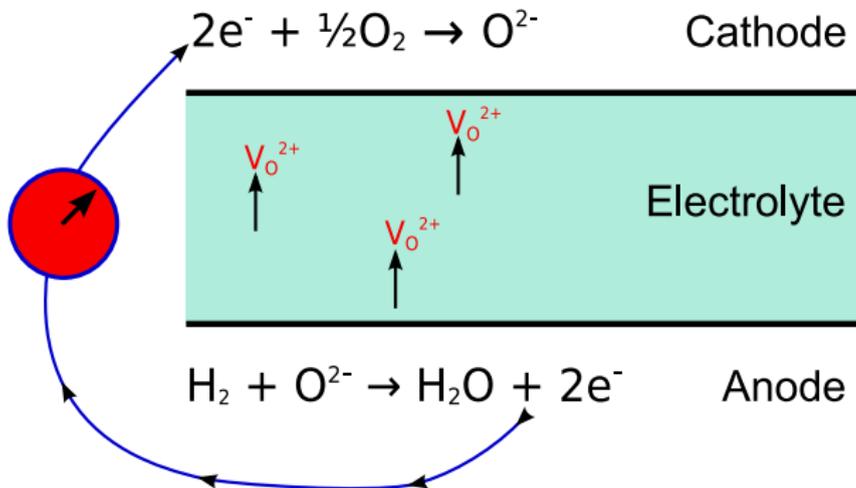
## Solid Oxide Fuel Cells



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## Solid Oxide Fuel Cells

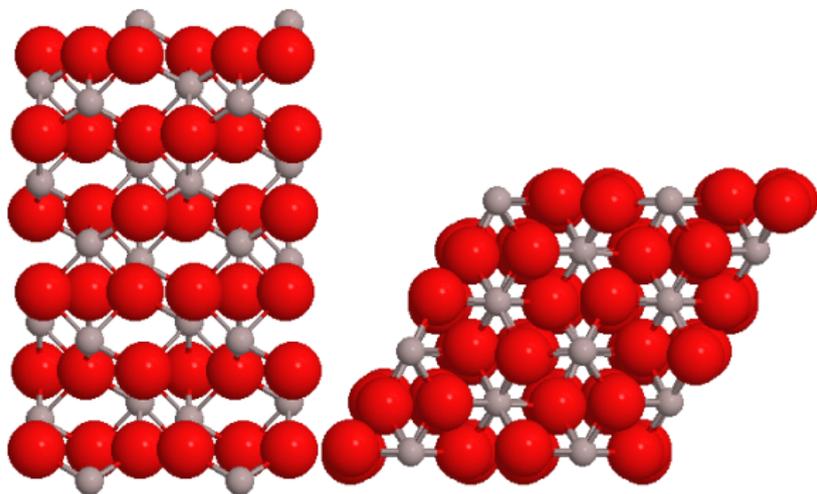


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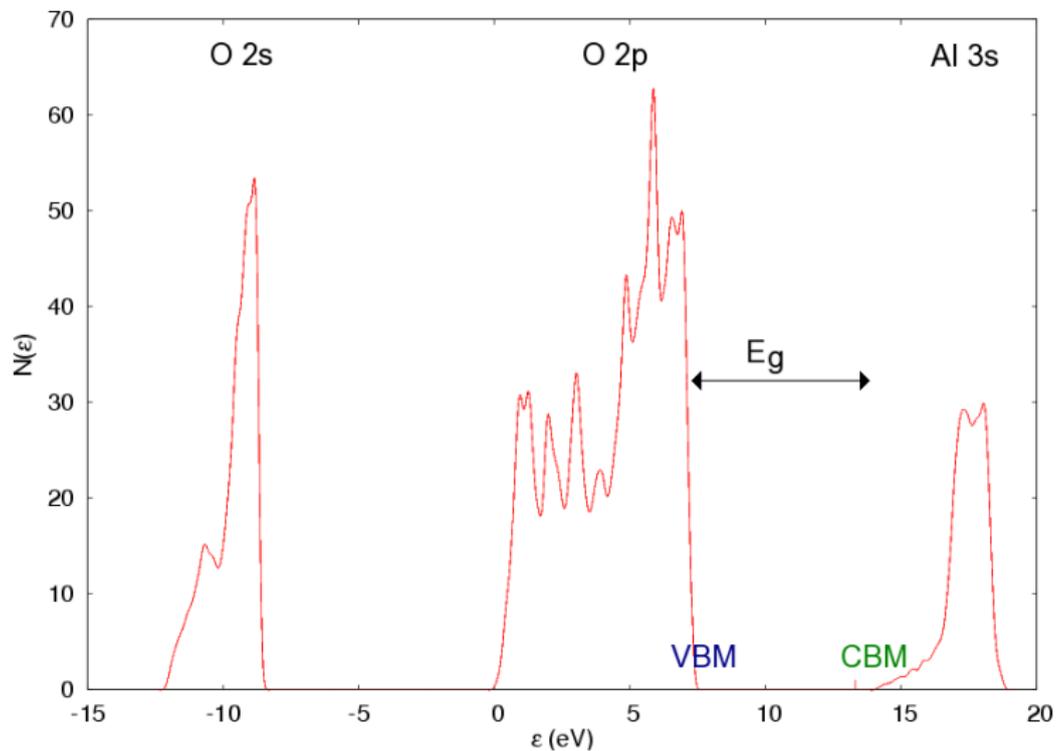
- 1 Why?
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  - The Perfect Crystal
  - Point Defects
  - Aliovalent Substitutional Defects
  - The Corundum Conundrum
- 3 Thermodynamics of Point Defects
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Complicated because of 2:3 coordination:



Supercell containing  $2 \times 2 \times 1$  copies of the hexagonal unit cell, with 120 atoms. Left: side view along the **a** axis. Right: top view down the **c** axis.

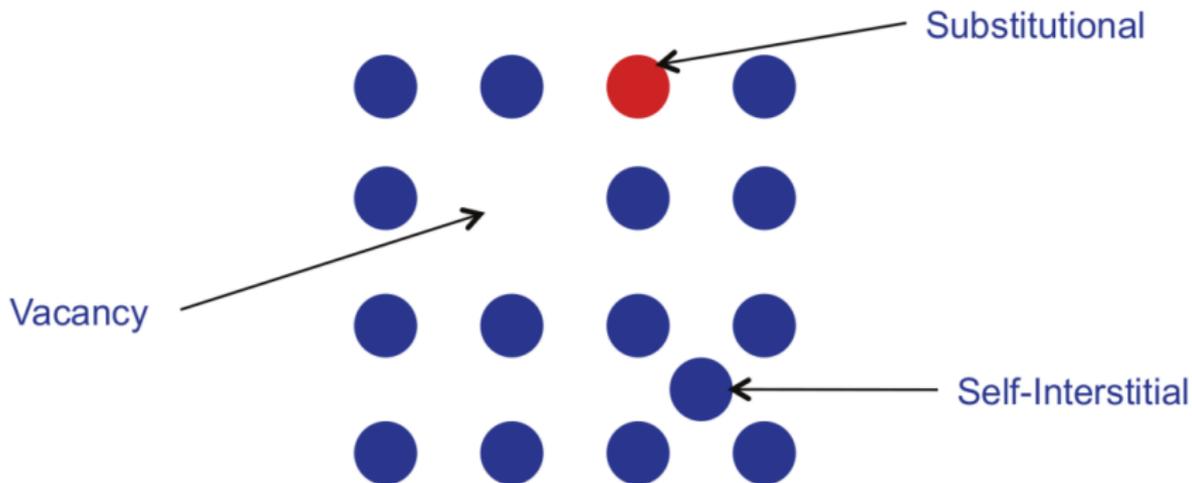
# Density of States



# Bonding and Electrical Properties

- Mainly ionic ( $\text{Al}^{3+}$  and  $\text{O}^{2-}$ ).
    - Clear from bandstructure.
    - Born effective charges close to +3 and -2.
- But with some covalent character.
- Point-charge and shell-model force fields do not work well.
  - Wide band gap ( $\sim 9\text{eV}$ ) insulator.
  - High dielectric constant ( $\sim 9$ ).

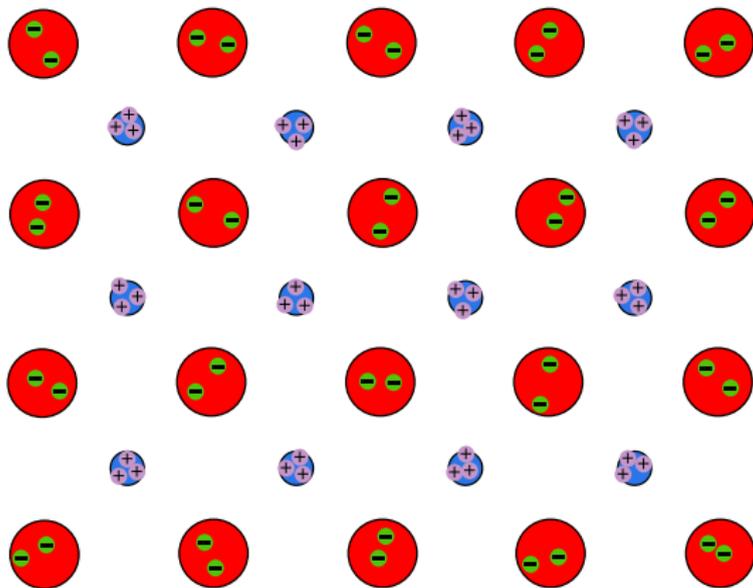
# Point Defect Types



Defects in insulators may exist in various charge states.

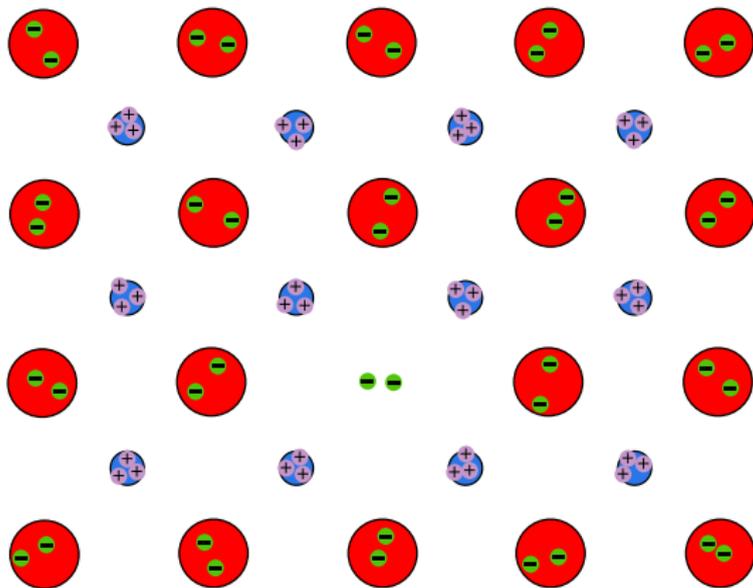
# Formation of Neutral O Vacancy

Perfect crystal



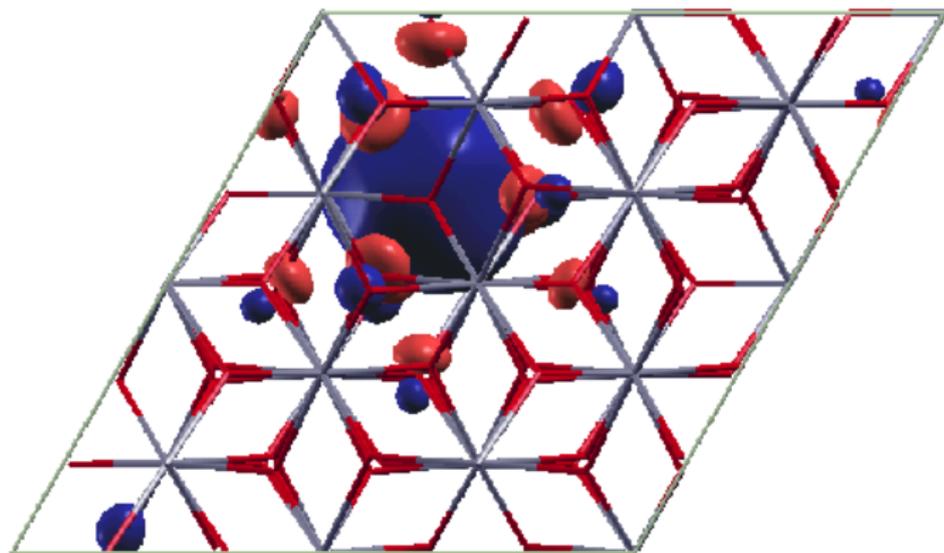
# Formation of Neutral O Vacancy

Remove neutral O atom, electrons remain behind  $\Rightarrow V_O$



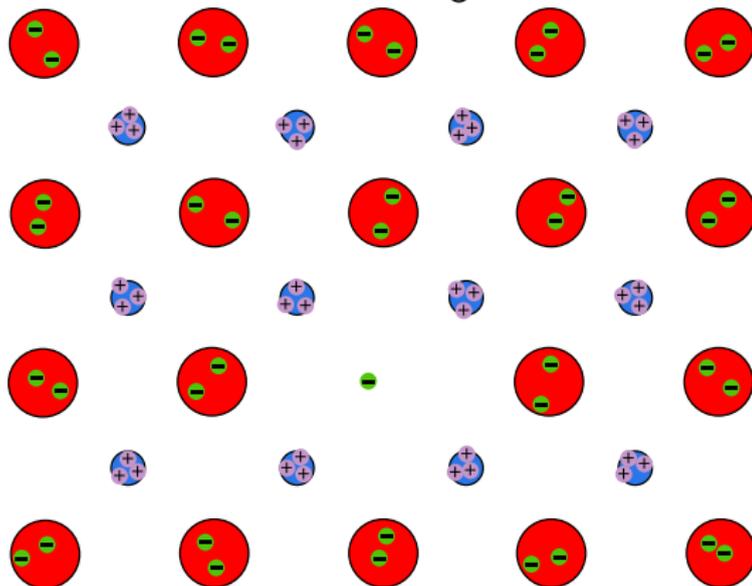
# Formation of Neutral O Vacancy

Localised orbital on neutral oxygen vacancy



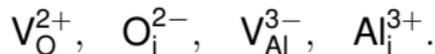
# Charged O Vacancies

Remove one localised electron  $\Rightarrow V_O^+$





- It is generally believed that native point defects in alumina have their full formal charges:

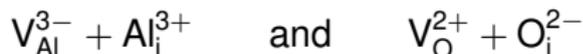


- Defects in **pure** alumina can only form in charge neutral combinations:

- Schottky (vacancies) and anti-Schottky (interstitials)



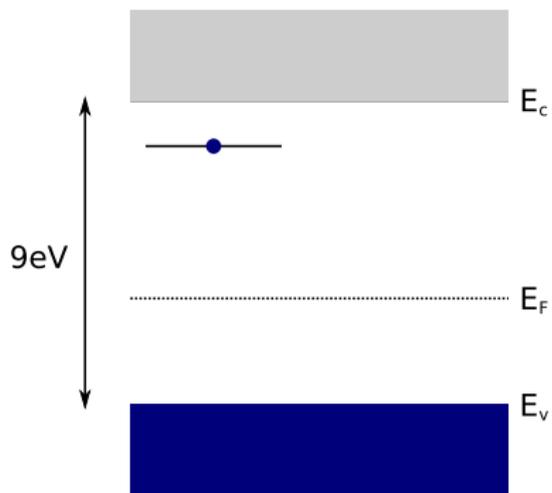
- Cation Frenkel ( $\text{Al}^{3+}$  ions) and anion Frenkel ( $\text{O}^{2-}$  ions)



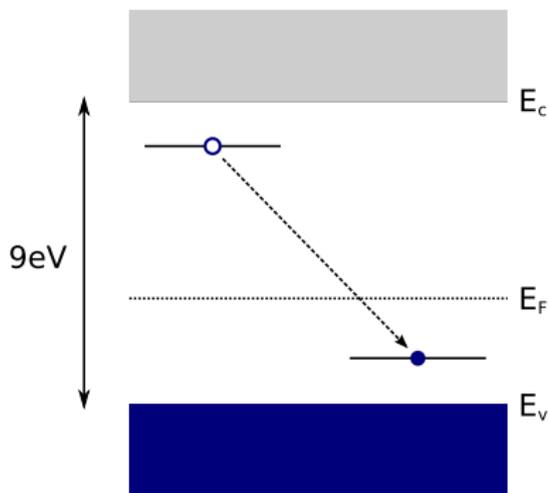
## $\text{Ti}_{\text{Al}}^{1+}$ Substitutional

- Replace a neutral Al atom (including the three valence electrons it had donated to nearby O atoms) by a neutral Ti atom.
- The Ti atom immediately donates 3 valence electrons to fill the 3 holes in the  $p$  orbitals on nearby O atoms. The defect as a whole remains neutral.
- The remaining Ti valence electron is left in a bound state high in the gap, well above  $E_F$ .

# Aliovalent Substitutional Defects



# Aliovalent Substitutional Defects

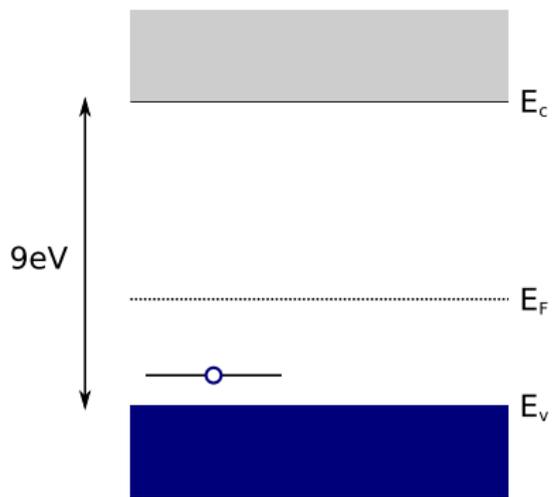


- Because the gap is large, the system can lower its total energy by creating a negatively charged native defect and moving the 4th Ti valence electron to that.
- $\text{Ti}_{\text{Al}}$  is a source of electrons, prompts the formation of negative defects, and increases  $E_F$ .

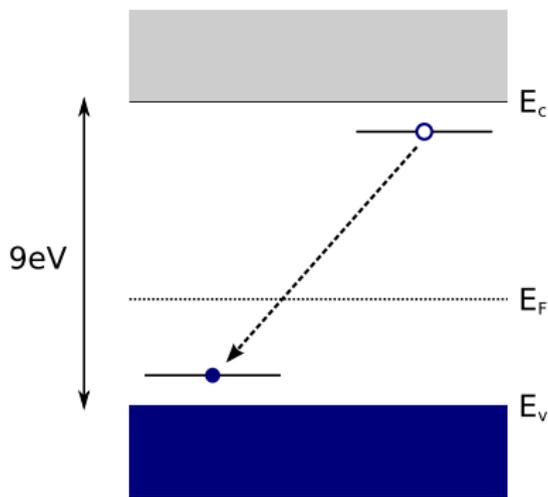
## $\text{Mg}_{\text{Al}}^{1-}$ Substitutional

- Replace a neutral Al atom (including the three valence electrons it had donated to nearby O atoms) by a neutral Mg atom.
- The Mg atom immediately donates its 2 valence electrons to fill 2 of the 3 holes in the  $p$  orbitals on nearby O atoms. The defect as a whole remains neutral.
- The remaining O  $p$  hole is left as a bound state above the bottom of the gap, below  $E_F$ .

# Aliovalent Substitutional Defects

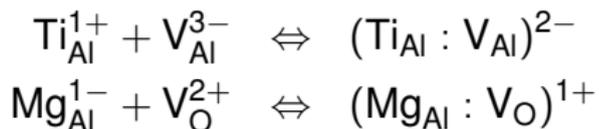


# Aliovalent Substitutional Defects



- Because the gap is large, the system can lower its total energy by creating a positively charged native defect and allowing the electron released to fill the O p hole.
- $Mg_{Al}$  is a source of holes, prompts the formation of positive defects, and decreases  $E_F$ .

- A substitutional impurity may bind to an intrinsic defect of opposite charge to form a defect cluster:



- Although the formation energies of such clusters are usually negative, configurational entropy wins and clusters dissociate at high enough  $T$ .

# The Corundum Conundrum

Despite widespread industrial usage, defect phenomena in  $\text{Al}_2\text{O}_3$  are not well understood or well controlled.

Diffusion experiments are our only experimental window to understanding, but low intrinsic concentrations, lack of a good radiotracer for Al, and unknown impurities content of samples limit interpretation of results.

Previous classical potential and DFT calculations produced formation energies very hard to reconcile with experimental  $E_a \sim 6\text{eV}$ .

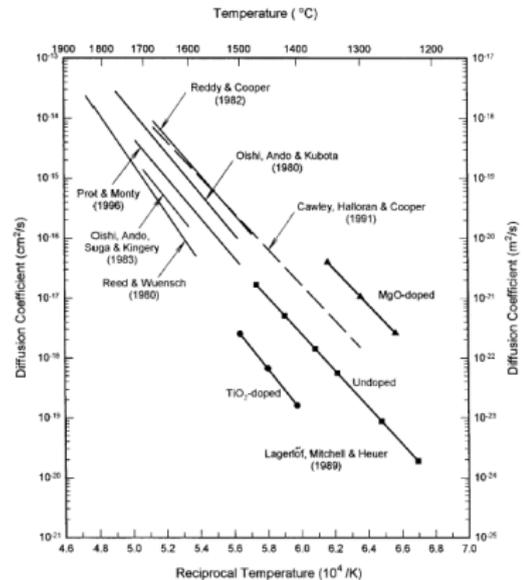


Figure 1. Oxygen diffusion data for undoped, MgO-doped and TiO<sub>2</sub>-doped  $\alpha\text{-Al}_2\text{O}_3$  from Lagerlöf *et al.* (1989), together with data for undoped  $\alpha\text{-Al}_2\text{O}_3$  from others in the period 1980–1996. See text for further details.

# The Corundum Conundrum

Some clear facts emerge from experiments

- $D_{\text{O}}$  is *smaller* than  $D_{\text{Al}}$  (or  $D$  for cation impurities) by several orders of magnitude.
- Rate-limiting  $D_{\text{loop}}$  sensitive to balance of aliovalent impurities. Up by  $\sim 100$  with 250ppm Mg; down by  $\sim 50 - 60$  with 600ppm Ti.
- However, given very low intrinsic native defect concentrations  $\sim 10^{-10}$ , these are remarkably small changes.

Could native defect concentrations somehow be “buffered” against doping? What role do defect clusters play? Can we predict diffusion coefficients *ab initio*?

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# Equilibrium Conditions

- Work at constant  $T$ ,  $P$ ,  $N_{\text{Al}}$ ,  $N_{\text{O}}$ ,  $N_{\text{Mg}}$ ,  $N_{\text{Ti}}$ .
- Equilibrium state minimises total Gibbs free energy

$$G = \sum_i N_i g_i - TS_{\text{config}}$$

- $N_i$  is number of formula units containing defects of type  $i$ . (Perfect formula unit included.)
- $g_i$  is Gibbs energy of crystal of  $N$  formula units containing one defect of type  $i$  minus Gibbs energy of perfect crystal of  $N - 1$  formula units. (Configurational entropy omitted.)
- 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.

Minimising

$$G = \sum_i N_i g_i - TS_{\text{config}}$$

subject to

- $\sum_i N_i n_i^{\text{Al}} = N_{\text{Al}}$
- $\sum_i N_i n_i^{\text{Mg}} = N_{\text{Mg}}$
- $\sum_i N_i = N$
- $\sum_i N_i n_i^{\text{O}} = N_{\text{O}}$
- $\sum_i N_i n_i^{\text{Ti}} = N_{\text{Ti}}$
- $\sum_i N_i q_i = 0$

yields ...

$$c_i = m_i \exp \left( - \frac{g_i - \mu_{\text{Al}} n_i^{\text{Al}} - \mu_{\text{O}} n_i^{\text{O}} - \mu_{\text{Mg}} n_i^{\text{Mg}} - \mu_{\text{Ti}} n_i^{\text{Ti}} + \mu_e q_i}{k_B T} \right)$$

- $c_i$  is the concentration of defects of type  $i$ .
- The  $\mu$ 's are Lagrange multipliers for the constraints.
- Sign of  $\mu_e$  chosen to allow us to interpret it as a chemical potential *for electrons*.
- $\Delta g_i = g_i - \mu_{\text{Al}} n_i^{\text{Al}} - \mu_{\text{O}} n_i^{\text{O}} - \mu_{\text{Mg}} n_i^{\text{Mg}} - \mu_{\text{Ti}} n_i^{\text{Ti}} + \mu_e q_i$  is called the **defect formation energy**.
- Since density of perfect formula units is almost 1:

$$g_{\text{Al}_2\text{O}_3} \approx 2\mu_{\text{Al}} + 3\mu_{\text{O}}$$

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  - Procedure
  - What Do We Need?
  - Methods
- 5 Results

# The Grand Canonical Ensemble

Although we have been working in the canonical ensemble so far, we now change viewpoints and treat  $\mu_{\text{O}}$ ,  $\mu_{\text{Al}}$ ,  $\mu_{\text{Mg}}$ ,  $\mu_{\text{Ti}}$ , and  $\mu_e$  as *inputs*.

- Imagine that the solid is in equilibrium with  $\text{O}_2$  gas at (partial) pressure  $P_{\text{O}_2}$  and temperature  $T$ :

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

- $\mu_{\text{Al}}$  is then determined using  $g_{\text{Al}_2\text{O}_3} \approx 2\mu_{\text{Al}} + 3\mu_{\text{O}}$ .
- $g_{\text{Al}_2\text{O}_3}$  will be calculated.

- Choose  $\mu_{\frac{1}{2}\text{O}_2}$  (and thus  $\mu_{\text{O}}$  and  $\mu_{\text{Al}}$ ).
- Choose  $\mu_e$ ,  $\mu_{\text{Mg}}$  and  $\mu_{\text{Ti}}$ .
- Calculate defect formation energies:
 
$$\Delta g_i = g_i - \mu_{\text{Al}} n_i^{\text{Al}} - \mu_{\text{O}} n_i^{\text{O}} - \mu_{\text{Mg}} n_i^{\text{Mg}} - \mu_{\text{Ti}} n_i^{\text{Ti}} + \mu_e q_i$$
- Obtain defect concentrations from Boltzmann equation:

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

- Adjust  $\mu_e$  until  $Q = 0$ .
- Adjust  $\mu_{\text{Mg}}$  and  $\mu_{\text{Ti}}$  to obtain required dopant concentrations.

# What Do We Need?

- 1 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

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

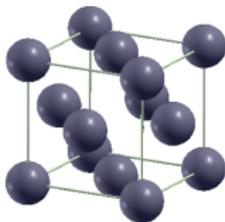
- The volume  $v$  and entropy  $s$  per molecule can be estimated using ideal gas formulae or obtained from thermodynamic tables.
- With a good quantum chemistry or QMC calculation, the total energy  $E_{\text{O}_2}$  of an oxygen molecule could be obtained accurately enough to be useful.
- But not in DFT . . .
- We use the Finnis-Lozovio-Alavi method to obtain values of  $\mu_{\text{O}_2}(P, T)$  that prove remarkably independent of pseudopotential or exchange-correlation functional.

# Gibbs Energies of Solids

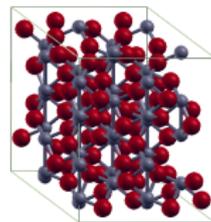
- For solids, PV contribution to  $G = U + PV - TS$  is negligible.
- In insulators, electronic excitation negligible. Obtain  $U_{\text{el}}$  from DFT or QMC ground-state total energy.
- Vibrational contributions to  $U$  and  $TS$  obtained from DFPT phonon calculations. Quantitatively but not qualitatively significant.



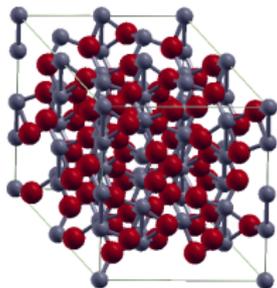
Oxygen molecule:  $E_T[\text{O}_2(g)]$



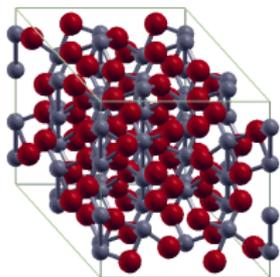
Aluminium metal:  $E_T[\text{Al}(s)]$



Alumina perfect crystal:  $E_T[\text{Al}_2\text{O}_3(s)]$

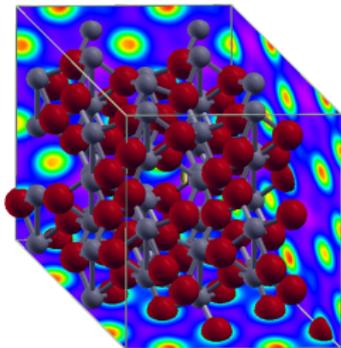


Aluminium vacancy:  $E_T^{def}[\text{V}_{\text{Al}}^q]$

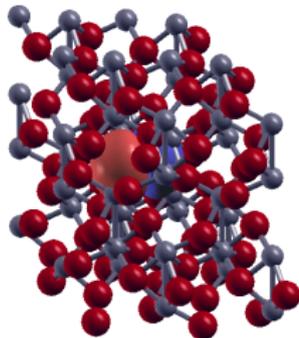


Aluminium interstitial:  $E_T^{def}[\text{Al}_I^q]$

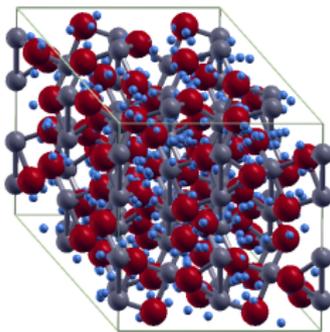
etc ...



Plane Wave DFT — CASTEP



Linear Scaling DFT — ONETEP



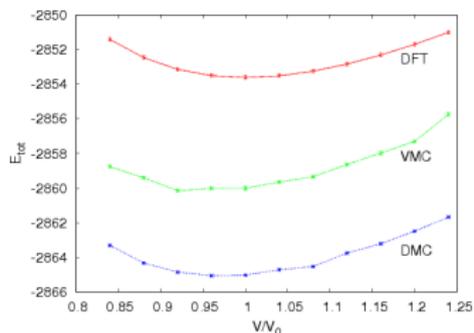
Diffusion Monte Carlo — CASINO

- 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 DFT calculation.
- Cells and supercells
  - $1 \times 1 \times 1$  hexagonal unit cell contains 30 atoms and 144 valence electrons.
  - The  $2 \times 2 \times 1$  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.

- Localised states in gap  $\Rightarrow$  self-interaction and band-gap problems in DFT (but not QMC).
  - Fortunately, the most important defects are  $V_{\text{Al}}^{3-}$  and  $V_{\text{O}}^{2+}$ , which do not have occupied states in the gap.
- Charged defects  $\Rightarrow$  enormous finite-size errors.
  - Careful extrapolation to infinite dilution required.
  - We use Nick Hine's clever Madelung extrapolation procedure. [Phys. Rev. B **79**, 024112 (2009)]

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  - Benchmarks
  - Defect Concentrations
  - Diffusion Coefficients

DMC lattice parameter is good:



Energy gap much closer to experiment than DFT:

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

# Formation Energies: DMC vs DFT

Previous DMC calculations of defects have suggested that DFT may overbind 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*

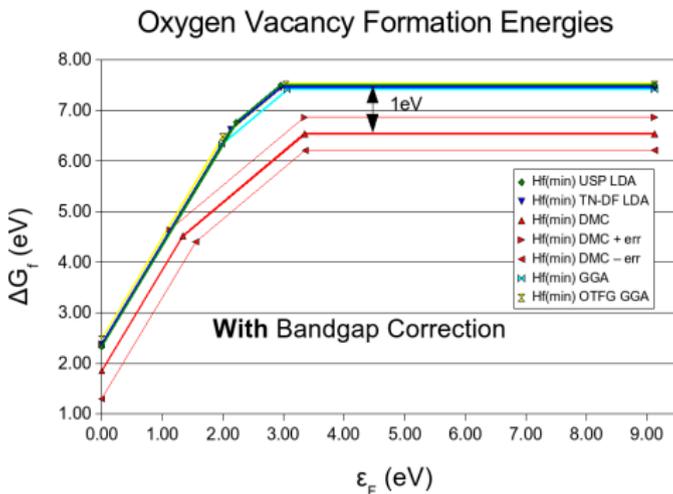
Vacancy formation energy 1eV lower in DMC than DFT.

Bonds cost too much to break/form in DFT.

⇒ Vacancy formation energies overestimated  
Interstitial formation energies underestimated

# Formation Energies: DMC vs DFT

$$\Delta g_i = g_i - \mu_{\text{Al}} n_i^{\text{Al}} - \mu_{\text{O}} n_i^{\text{O}} + \mu_e q_i$$



$V_{\text{O}}^0$  and  $V_{\text{O}}^{1+}$  (both of which have electrons in localised states on the defect site) are too difficult to form in DFT (self-interaction?). Error in  $V_{\text{O}}^{2+}$  formation energy is smaller.

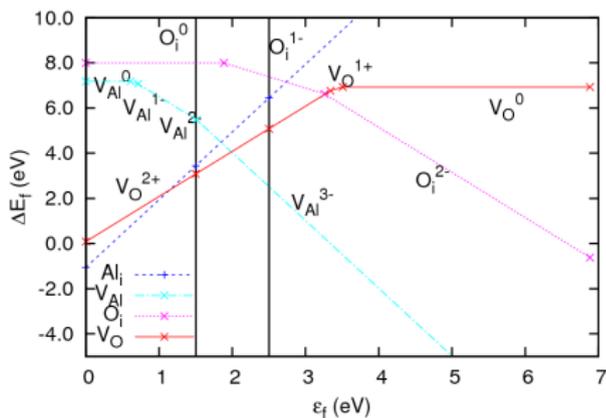
# Is DFT Good Enough?

The most important defects,  $V_O^{2+}$ ,  $V_{Al}^{3-}$ ,  $O_i^{2-}$ ,  $Al_i^{3+}$ , all have full ionic charges and no occupied states in the gap. Errors in DFT formation energies  $\leq 0.5$  eV. ( $k_B T = 0.15$  eV at 1750K).

We'll assume that DFT is good enough from now on.

# Formation Energies

- First step is to choose a  $T$  and calculate the formation energies of all possible contributing defects and clusters as functions of  $\mu_e$ ,  $\mu_{\text{Mg}}$  and  $\mu_{\text{Tj}}$ .



Most papers stop here — but no use to experimentalists yet ...

# Self-Consistent Concentrations

- Next step is to use Boltzmann factor

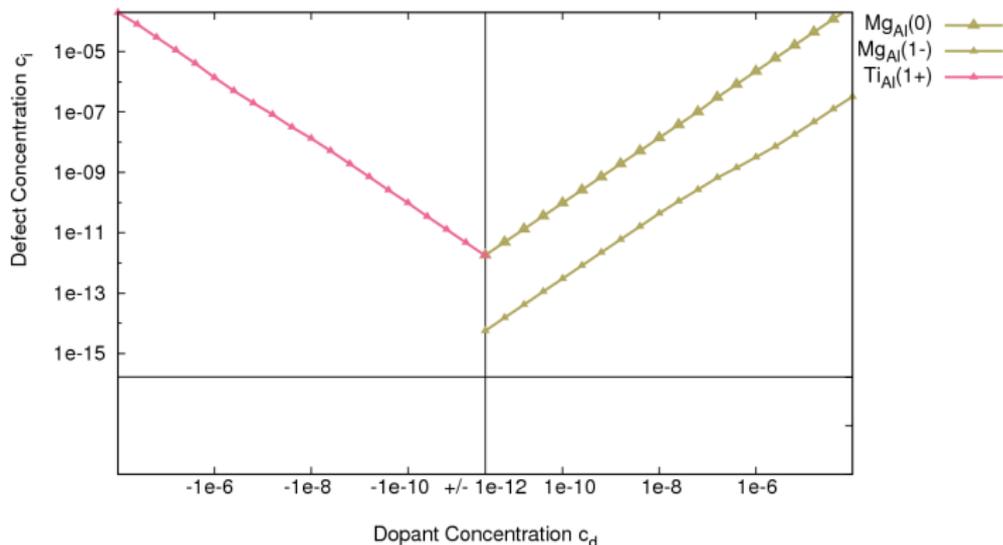
$$c_i = m_i \exp \left( - \frac{g_i - \sum_{\alpha} \mu_i^{\alpha} n_i^{\alpha} + \mu_e q_i}{k_B T} \right)$$

to calculate concentrations of all defects as functions of  $\mu_e$ ,  $\mu_{Mg}$  and  $\mu_{Ti}$ .

- Adjust  $\mu_{Mg}$  and  $\mu_{Ti}$  to obtain desired doping levels and  $\mu_e$  to ensure charge neutrality.
- Dependence of concentrations on  $\mu_e$ ,  $\mu_{Mg}$  and  $\mu_{Ti}$  builds in a mean-field-like coupling between populations of different types of defects.

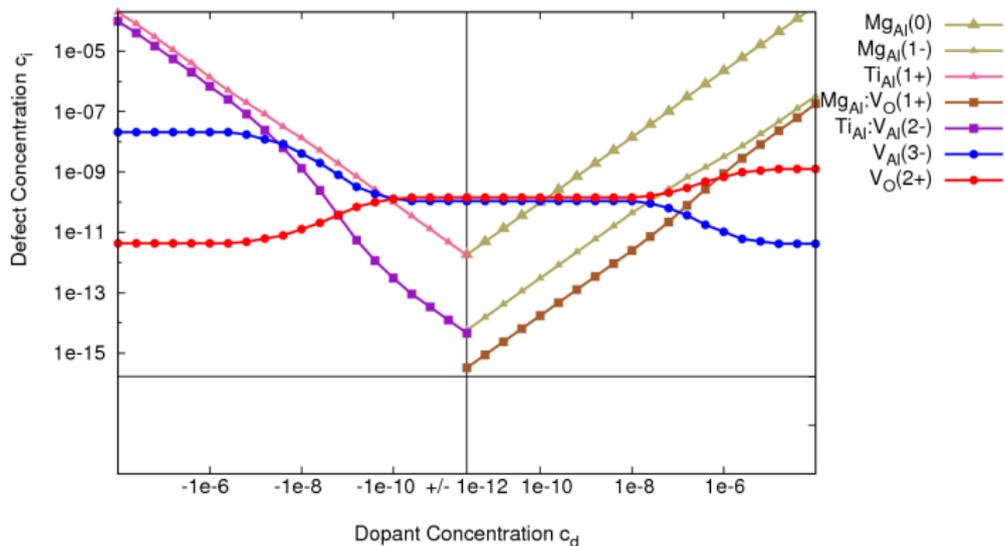
# Self-Consistent Concentrations

Concentrations of substitutionals with increasing doping.



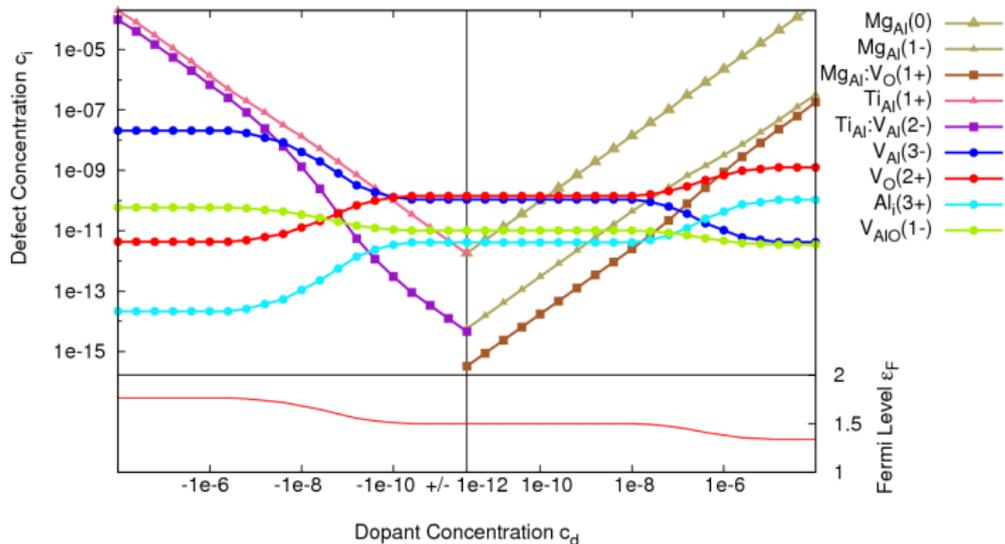
# Self-Consistent Concentrations

Concentrations of substitutionals, vacancies and clusters.



# Self-Consistent Concentrations

Concentrations of all significant defects, and Fermi level.



# The Law of Mass Action

- Consider, for example, the reaction



- Define  $\Delta g_b$  by

$$\Delta g_{(\text{Mg}_{\text{Al}} : \text{V}_{\text{O}})^{1+}} = \Delta g_{\text{Mg}_{\text{Al}}^{1-}} + \Delta g_{\text{V}_{\text{O}}^{2+}} + \Delta g_b$$

- Exponentiating gives

$$\exp\left(-\frac{\Delta g_{(\text{Mg}_{\text{Al}} : \text{V}_{\text{O}})^{1+}}}{k_B T}\right) = \exp\left(-\frac{\Delta g_b}{k_B T}\right) \exp\left(-\frac{\Delta g_{\text{Mg}_{\text{Al}}^{1-}} + \Delta g_{\text{V}_{\text{O}}^{2+}}}{k_B T}\right)$$

# The Law of Mass Action

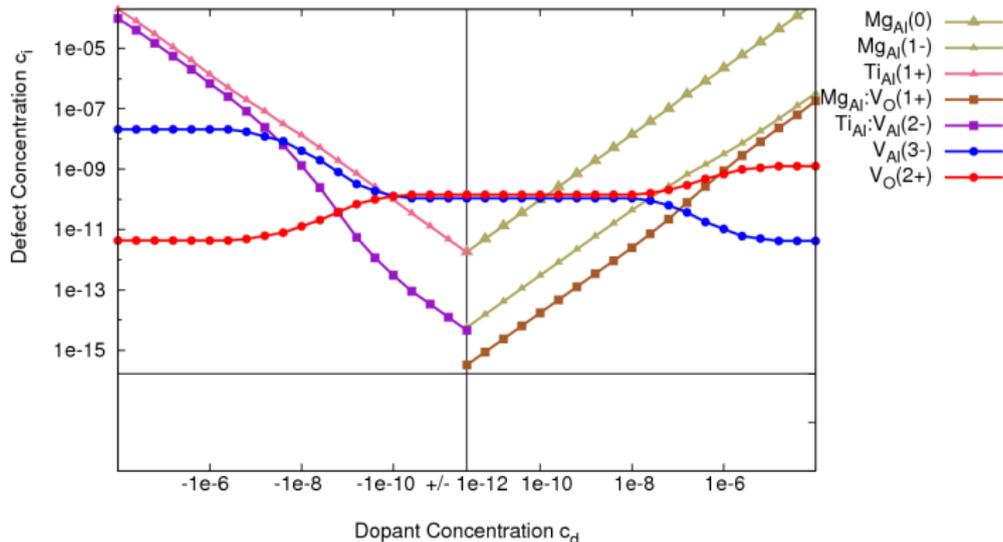
$$\exp\left(-\frac{\Delta g_{(\text{Mg}_{\text{Al}}:\text{V}_{\text{O}})^{1+}}}{k_B T}\right) = \exp\left(-\frac{\Delta g_b}{k_B T}\right) \exp\left(-\frac{\Delta g_{\text{Mg}_{\text{Al}}^{1-}} + \Delta g_{\text{V}_{\text{O}}^{2+}}}{k_B T}\right)$$

- This leads to the Law of Mass Action

$$[(\text{Mg}_{\text{Al}}:\text{V}_{\text{O}})^{1+}] = \frac{1}{k_0} \exp\left(-\frac{\Delta g_b}{k_B T}\right) [\text{Mg}_{\text{Al}}^{1-}][\text{V}_{\text{O}}^{2+}]$$

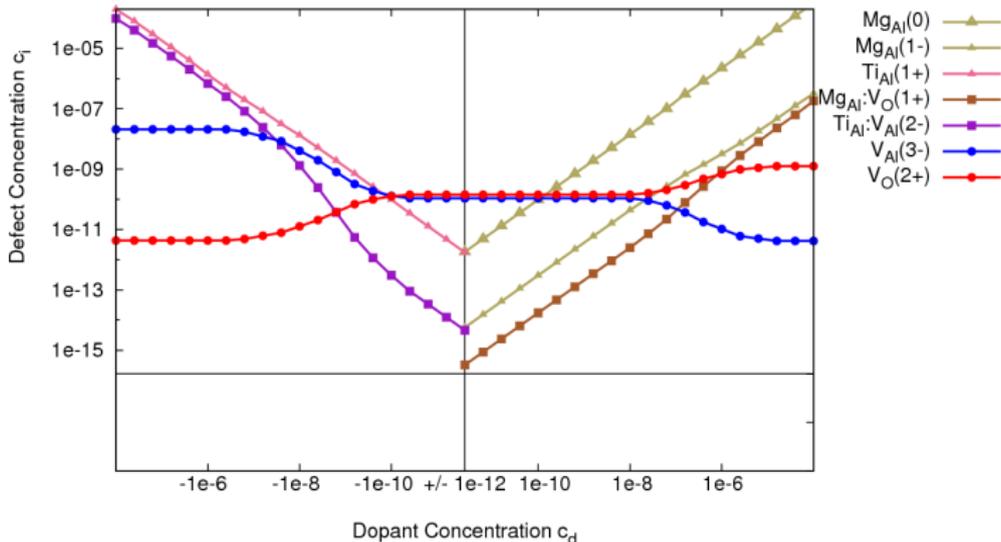
where  $k_0$  is the ratio of multiplicities.

# Buffering Explained



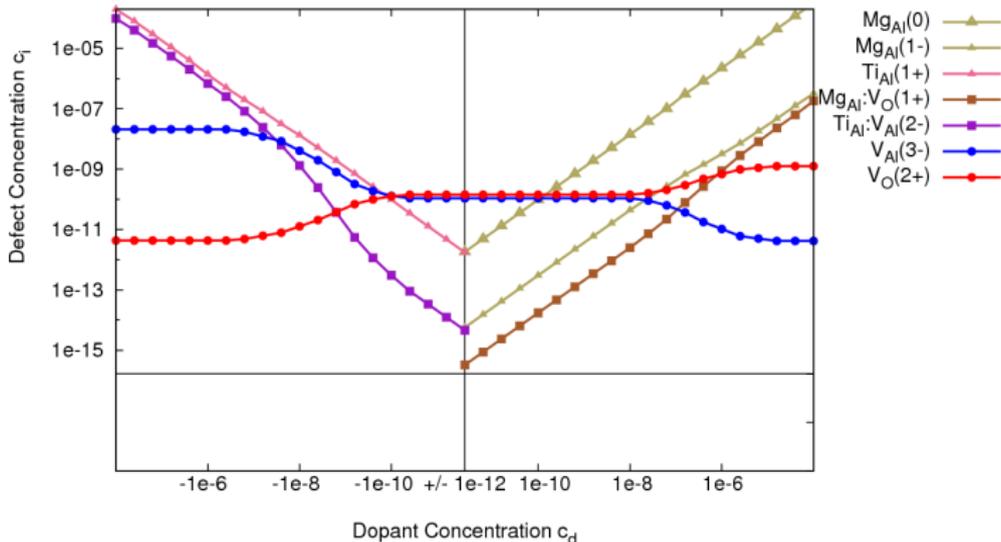
- Near zero doping, Fermi level adjusts itself such that  $[V_O^{2+}] \approx 3[V_{Al}^{3-}]/2$ .

# Buffering Explained



- As  $[Mg_{Al}^{1-}]$  rises, Fermi level drops slightly,  $[V_O^{2+}]$  rises slightly, and  $[V_{Al}^{3-}]$  drops slightly, maintaining charge neutrality. (Rise is too small to see on the log scale of the graph.)

# Buffering Explained

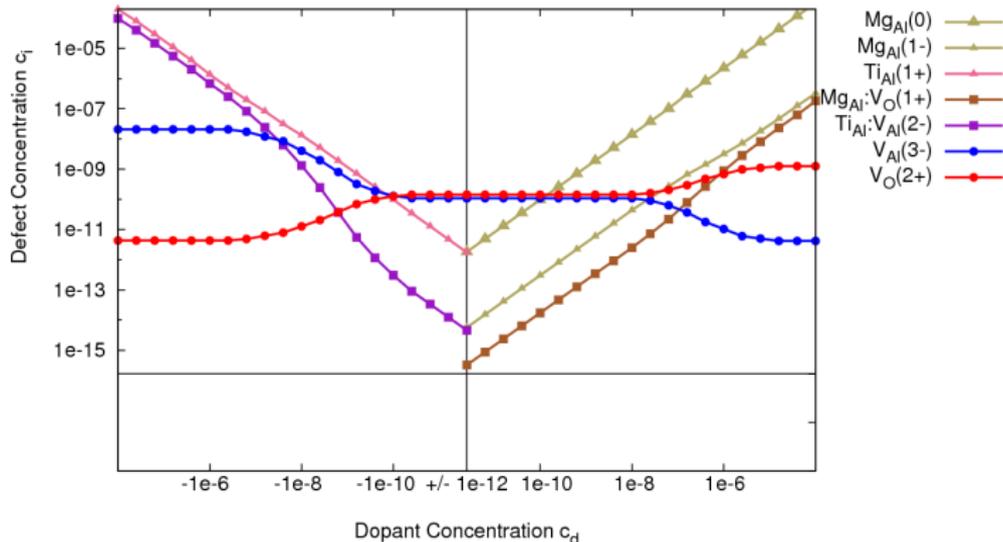


- According to the law of mass action,

$$[(Mg_{Al} : V_O)^{1+}] = K(T) [Mg_{Al}^{1-}] [V_O^{2+}].$$

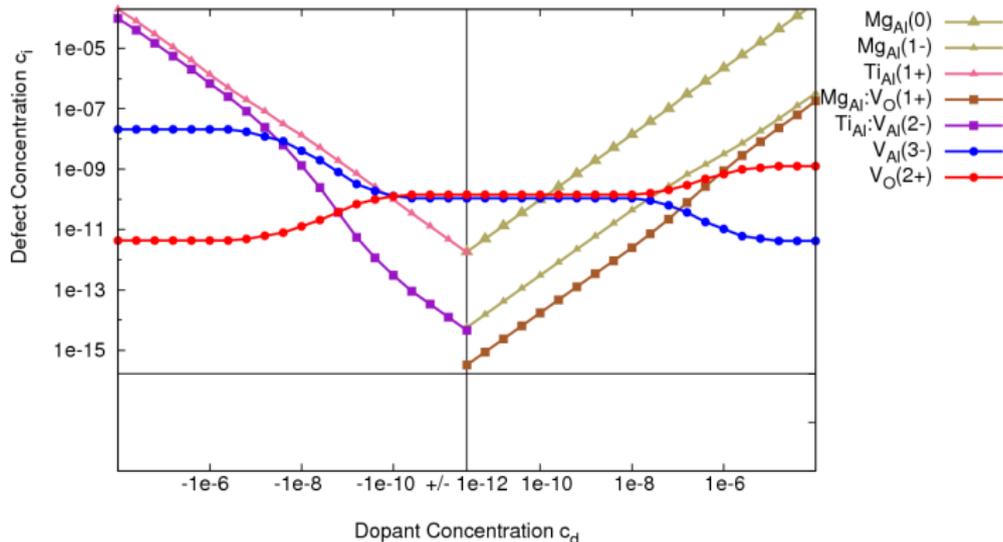
Increasing  $[Mg_{Al}^{1-}]$  and  $[V_O^{2+}]$  thus increases  $[(Mg_{Al} : V_O)^{1+}]$ .

# Buffering Explained



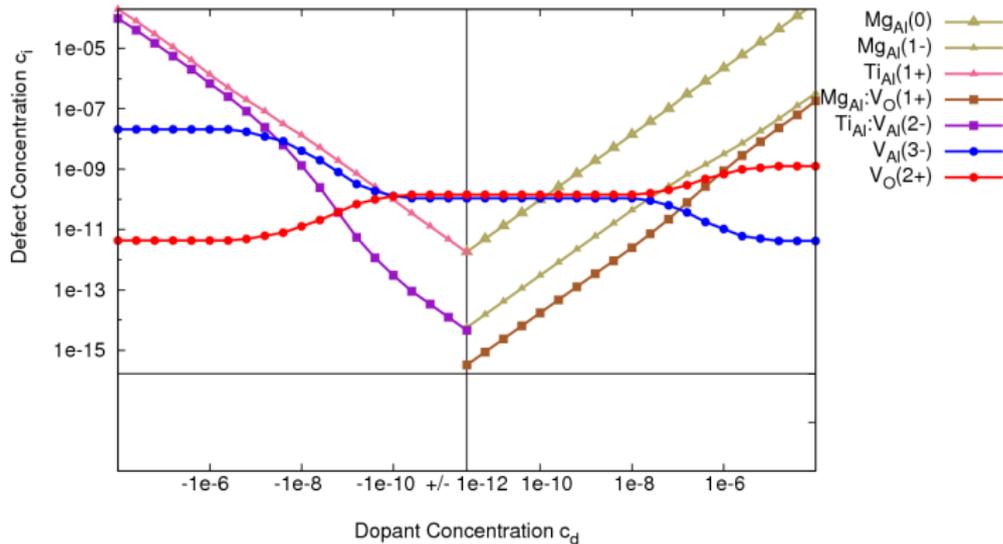
- At high enough doping,  $[(Mg_{Al} : V_O)^{1+}]$  exceeds  $[V_O^{2+}]$  and the further creation of  $V_O^{2+}$  defects is unnecessary.

# Buffering Explained



- The Fermi level settles down such that one new  $(Mg_{Al} : V_O)^{1+}$  defect is formed for every  $Mg_{Al}^{1-}$  defect added.

# Buffering Explained



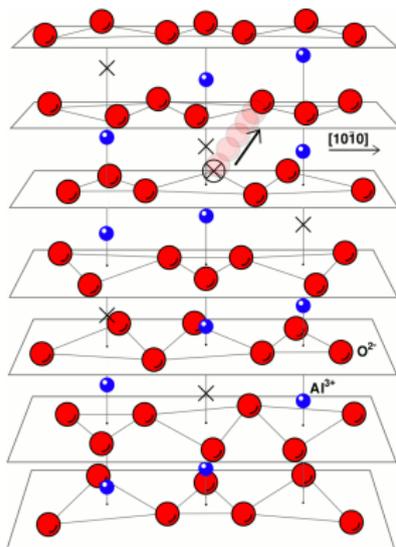
- The  $V_O^{2+}$  and  $V_{Al}^{3-}$  concentrations are buffered and no longer change.

# DFT Migration Barriers

Move atoms step by step  
from one possible site to an  
adjacent one

Constrain atom to series of  
planes perpendicular to  
vector joining start and end  
points.

Relax all atoms fully at each  
fraction along vector.

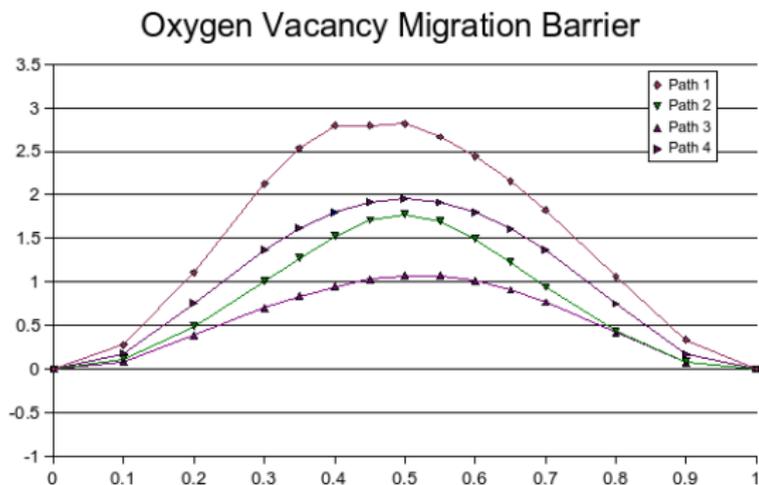


# DFT Migration Barriers

Migration barriers to site-to-site diffusion of oxygen vacancy

Different paths show very different barriers.

Lowest barriers  $\sim 1\text{eV}$  only permits movement around smaller triangles of  $\text{O}^{2-}$  ions. Real barrier to 3D diffusion is  $\sim 1.73\text{eV}$ .

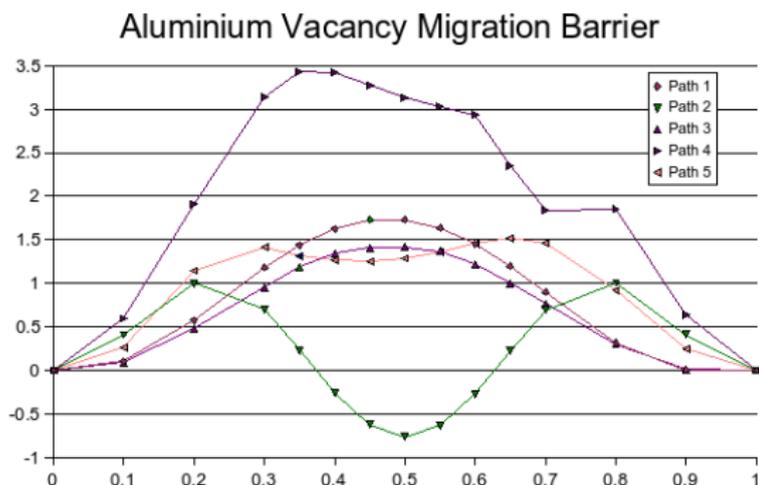


# DFT Migration Barriers

Migration barriers to site-to-site diffusion of aluminium vacancy

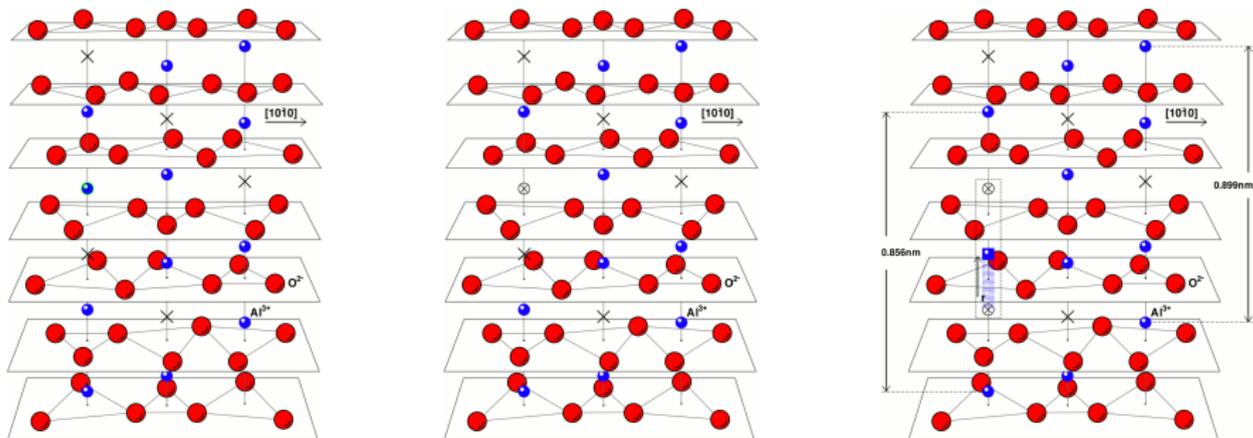
Revealed an unexpected new configuration (of notably lower energy)

Split vacancy along c-axis.



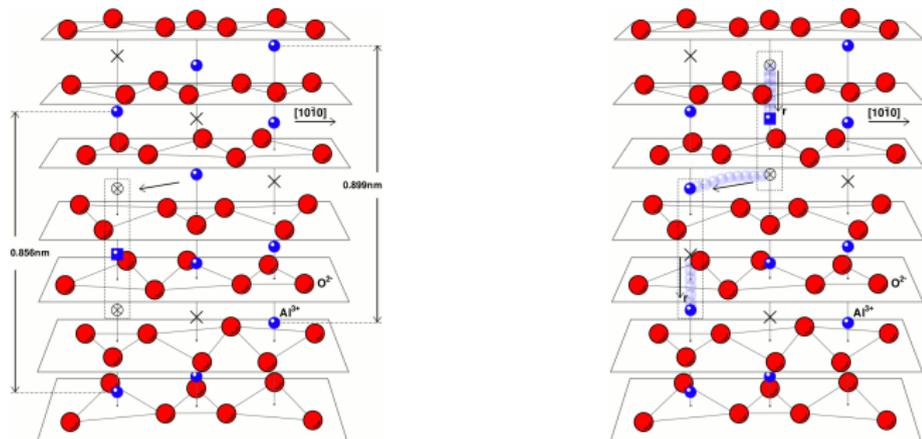
# Split Aluminium Vacancy

Can be thought of as 2 vacancies and 1 interstitial ...



# Split Aluminium Vacancy Migration

Moves in complex correlated motion of several atoms.



Overall barrier is relatively low.

Summary of migration barriers for intrinsic defect species:

Defect Species	$\Delta E_{\text{mig}}$ (eV)
$V_{\text{O}}^{2+}$	1.73
$V_{\text{Al}}^{3-}$	1.27
$\text{Al}_i^{3+}$	1.31
$\text{O}_i^{2-}$	0.69
$V_{\text{AlO}}^{1-}$	2.35

Reasonably in line with expectations of ceramicists (much lower than previous DFT estimates — which presumably did not find the fully relaxed path).

# Calculating Diffusion Coefficients

Diffusion coefficients  $D_i$  given by Arrhenius equation:

$$D_i = D_0 e^{-E_i^a/k_B T}$$

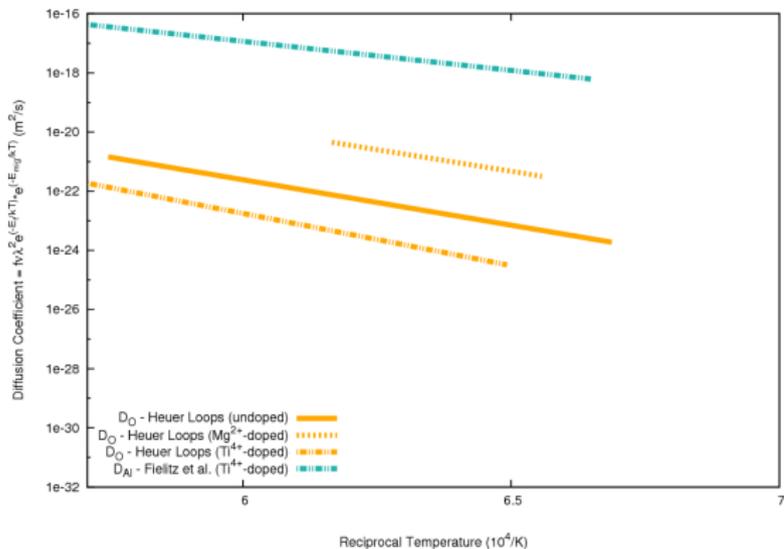
where the activation energy  $E_i^a$  is the sum of the migration energy and the formation energy.

Pre-exponential factor  $D_0 \propto f\alpha^2\nu$ .

- $f$ : correlation factor (calculate from structure)
- $\alpha$ : jump distance (estimate from bond lengths)
- $\nu$ : attempt frequency (estimate from phonon frequencies)

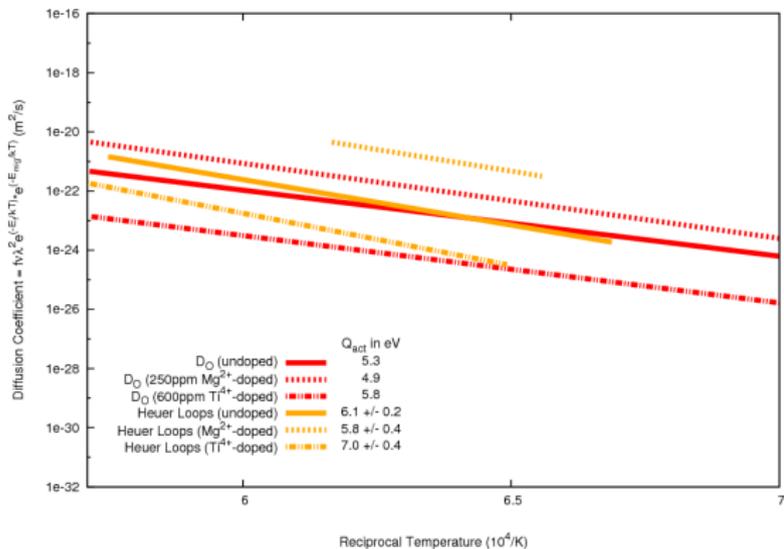
# Reliable Experimental Diffusion Measurements

## Loop annealing Data (Heuer), Al Tracer data (Fielitz)



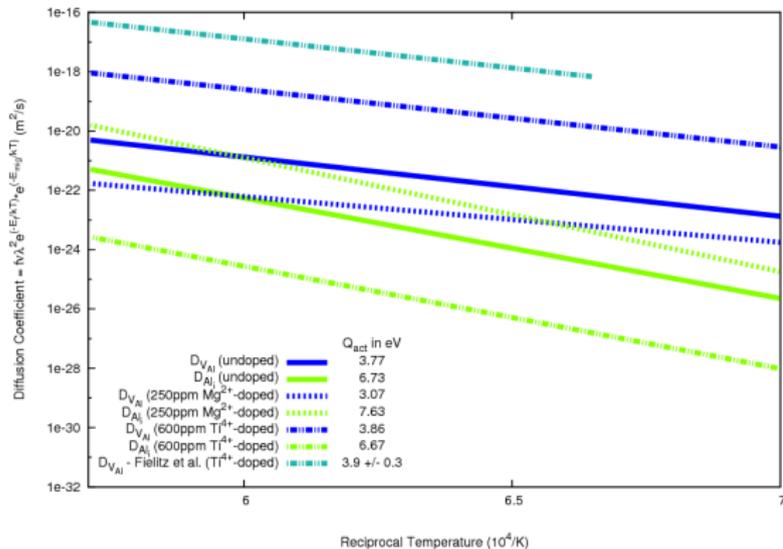
# Oxygen Diffusion Coefficients

Calculated vs Experimental diffusion coefficients for  $V_O^{2+}$ .



# Aluminium Diffusion Coefficients

Calculated vs Experimental diffusion coefficients for  $V_{Al}^{3-}$  and  $Al_i^{3+}$ .



'Buffering' effect observed under aliovalent doping in oxygen and aluminium diffusion coefficient explained in terms of movement of Fermi level with changing ratios of concentrations of substitutionals relative to intrinsic defects and clusters.

Predicted and observed activation energies reconciled: good quantitative predictions of diffusion coefficients possible in ceramics.

- 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  $\Rightarrow$  opportunities for QMC.