ESP5403 Nanomaterials for Energy Systems

Ionic Conductors

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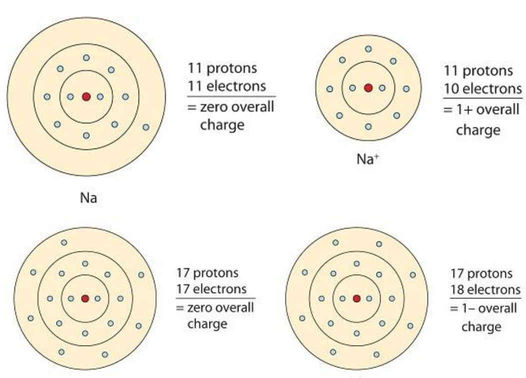
Ionic Bonding

Ionic bonding is the complete transfer of valence electron(s) between atoms. It is a type of chemical **bond** that generates two oppositely charged **ions**. In **ionic bonds**, the metal loses electrons to become a positively charged cation, whereas the nonmetal accepts those electrons to become a negatively charged anion.



Ionic Conductivity

$$\sigma = \frac{1}{k_B T} \cdot \sum_i (Z_i q)^2 \, n_i D_i$$

- Conductivity is influenced by 1)the carrier concentration n, 2) the carrier mobility μ
- Usually, defects act as the charge carriers
  - not many defects in most ionic solids
  - mobility is usually low at room temperature

	Material	Conductivity (S m^{-1})
Ionic conductors	Ionic crystals	$< 10^{-16} - 10^{-2}$
	Solid Electrolytes	10^{-1}-10^{3}
	Liquid electrolytes	10^{-1}-10^{3}
Electronic conductors	Metals	10^{3}-10^{7}
	Semiconductors	10^{-3}-10^{4}
	Insulators	$< 10^{-10}$

Ionic Conduction in Solids

$$\sigma_{ion} = n\, Z_i\, q\, \mu$$

$$= n\, Z_i q\, \frac{Z_i q}{kT} D$$

$$D = D_0 \exp\left(\frac{-\Delta G}{k_B T}\right)$$

$$= \gamma(1-c) Z a^2 \nu_0 \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(\frac{-E_m}{k_B T}\right)$$

$$\sigma_{ion} = n\, Z_i q\, \frac{Z_i q}{kT} D_o\, exp\left(\frac{-\Delta G}{kT}\right)$$

$$\sigma_{ion} = Nc\, \frac{(Z_i q)^2}{kT}\; D_o\, exp\left(\frac{-\Delta G}{kT}\right)$$

$$\sigma_{ion} = Nc\, \frac{(Z_i q)^2}{kT} \gamma(1-c).Z a^2 \nu_o\, exp\left(\frac{\Delta S}{k}\right) exp\left(\frac{-E_m}{kT}\right) \quad (1)$$

$$\sigma_{ion} = \frac{\sigma_o}{T} exp\left(\frac{-E_m}{kT}\right) \quad (2)$$

Where, *n* is the carrier density (#/cm^3), μ the mobility (cm^2/Vs), and $Z_i q$ the charge (q = 1.6x10^{-19} C) of the i^{th} charge carrier. The huge (many orders of magnitude) differences in between metals, semiconductors and insulators generally result from differences in *n* rather than μ. On the other hand, the higher conductivities of electronic versus ionic conductors are generally due to the much higher mobilities of electronic versus ionic species.

Charge number or valence of an ion is the coefficient that, when multiplied by the elementary charge, gives the ion's charge. For example, the charge on a chloride ion, Cl^-, is − 1 · *q*, where *q* is the elementary charge. This means that the charge number for the ion is − 1.

Ionic Conduction in Solids

- This expression (1) shows that σ_{ion} is nonzero only when the product *c(1-c)* is nonzero. Since all normal sites are fully occupied (*c* = 1) and all interstitial sites are empty in a perfect classical crystal, this is expected to lead to highly insulating characteristics.

- The classical theory of ionic conduction in solids is thus described in terms of the creation and motion of atomic defects or point defects, notably vacancies and interstitials.

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- For ionic crystals, ionic conduction is mainly intrinsic because the crystals have thermally created vacant sites in the lattice through which ions can move. The simplest types of thermally created vacant sites (lattice defects) are the well known Frenkel and Schottky defects shown in Figure (see next slide).

- Frenkel defect is formed when an ion originally at a lattice site moves to an interstitial position, which implies that this process generates two imperfections: a vacancy in the lattice and an interstitial ion.

- A Schottky defect is formed when an ion originally at a lattice site diffuses to a surface position, creating one imperfection: a vacancy in the lattice. Since the volume and the surface of a crystal must be electrically neutral, Schottky defects must be created in pairs: one vacancy created by displacing an anion and the other by displacing a cation.

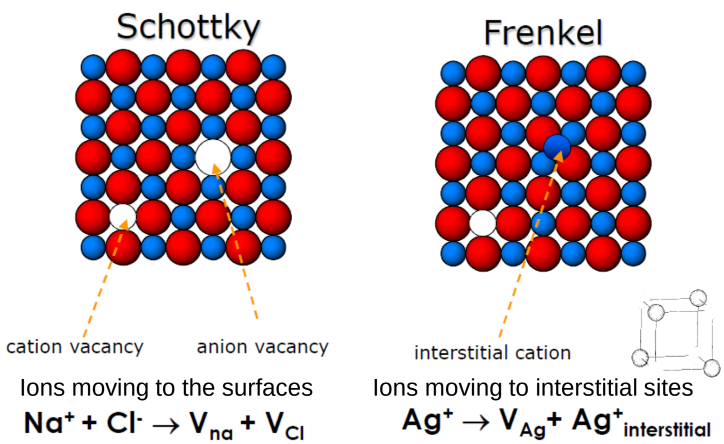
- In most alkali halide ionic crystals, probability of the formation of the Schottky defects is much higher than that of the Frenkel defects. It can be imagined that in large ions, vacant lattice sites must be present for the ionic movement, whereas small ions can move through the interstitial space.

- For non-ionic solids, some structures may provide channels, which allow the ions some space to move.

Ionic Conductors: Point Defects

A Point Defect involves missing of a single atom in the normal crystal array.

There are three types of point defects: Vacancies. Interstitial and Impurities. They may be built-in with the original crystal growth.



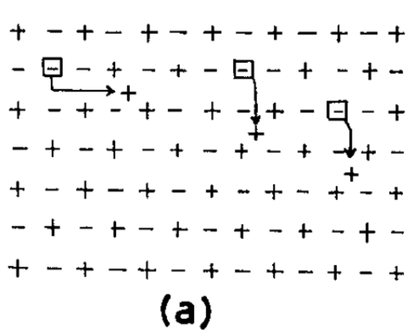
Schematic representations of Schottky defects and Frenkel defects

Point Defects

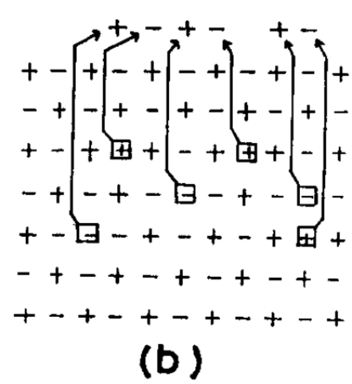
Point defect type of solids is further subdivided into two, according to the defect concentration.

(a). Diluted. n <<10^{18}/cm^3 , **e.g.:** NaCl, KCl, AgCl, etc.

(b). Concentrated. n=~ 10^{20}/cm^3', **e.g.:** ZrO_2, CaF_2, etc



Frenkel defects formation



Schottky defects formation

Molten Sub-lattice

In molten sub-attice type solids, all ions are available for conductions, since the number of defects or void sites in the sub-lattice are more than the number of ions. So, ions can move freely from one position to another with low activation energy possessing high conductivity is called superionic conductors (SICS).

Ionic Solids Classification

(i). Conventional ionic solids, in which the defect concentration is low. The numbers of mobile defects are – $10^{18}/cm^3$ or less. These are same as "dilute type point defect".

(ii) These are same as concentrated type point defect. The defect concentration is - $10^{20}/cm^3$.

(iii). These are the "molten sub-lattice type", in which all the ions in a sub-lattice are available for movement. The numbers of mobile ionic charge carriers are - $10^{22}/cm^3$

In order to increase the conductivity of an ionic solid, we need to:
1). Raise the temperature and so increase the number of intrinsic defects; or
2). Add an impurity to create vacancies or defects in the structure (extrinsic defects); or
3). Lower the activation energy of the jump, perhaps by creating more space in the structure.

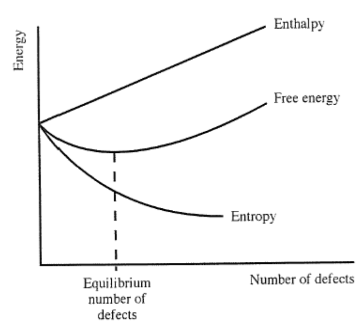
Concentration of Intrinsic Defects: Schottky Defects

Energy is required to form a defect (endothermic process)

Although there is a cost in ***energy***, there is a gain in ***entropy*** in the formation of a defect.

At equilibrium, the overall change in free energy of the crystal due to the defect formation is zero according to:

$$\Delta G = \Delta H - T\Delta S$$



At any temperature, there will always be an equilibrium population of defects. The number of defects (for an MX crystal) is given by:

$$n_s \approx N \exp\left(\frac{-\Delta H_s}{2kT}\right)$$

where n_s is the number of Schottky defects per unit volume, at T K, in a crystal with N cations and N anion sites per unit cell volume, and ΔH_s is the enthalpy required to form one defect.

Recall:

What are Gibbs Free energy, Enthalpy and Entropy?

At what condition does a reaction forming a product from the reactants proceed spontaneously?

At what condition does the equilibrium exists between reactants and product?

At what condition does the reaction is non-spontaneous?

What is standard condition for thermodynamic reactions?

https://www.youtube.com/watch?v=-UI8c_ot4j0

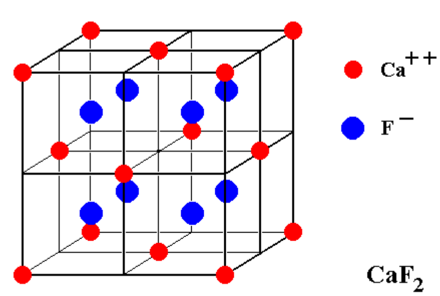
https://www.youtube.com/watch?v=XvuRJuXykyw

Anion Frenkel Defect in Fluorite

Cation Frenkel defects are common because of the typically smaller size of a cation compared to an anion.

However, anions in the fluorite structure have a lower electrical charge than the cations and don’t find it as difficult to move nearer each other.

The fluorite structure ccp cations with all tetrahedral holes occupied by the anions – thus all octahedral holes are unoccupied.



Concentration of Defects, cont.

Consider a MX crystal, the number of Frenkel defects present in this crystal is:

$$n_f \approx (NN_i)^{1/2} \exp\left(\frac{-\Delta H_F}{2kT}\right)$$

where n_f is the number of Frenkel defects per unit volume, N is the number of lattice sites, and N_i the number of interstitial sites available., and ΔH_F is the enthalpy of formation of one Frenkel defect.

If ΔH_F is the enthalpy of formation of one mole of Frenkel defects:

$$n_f \approx (NN_i)^{1/2} \exp\left(\frac{-\Delta H_F}{2RT}\right)$$

Knowing the enthalpy of formation for Schottky and Frenkel defects, one can estimate how many defects are present in a crystal.

Concentration of Defects, cont.

Schottky Defects

Compound	ΔH (10^{-19} J)	ΔH (eV)
MgO	10.57	6.60
CaO	9.77	6.10
LiF	3.75	2.34
LiCl	3.40	2.12
LiBr	2.88	1.80
LiI	2.08	1.30
NaCl	3.69	2.30
KCl	3.62	2.26

Frenkel Defects

Compound	ΔH (10^{-19} J)	ΔH (eV)
UO_2	5.45	3.40
ZrO_2	6.57	4.10
CaF_2	4.49	2.80
SrF_2	1.12	0.70
AgCl	2.56	1.60
AgBr	1.92	1.20
β-AgI	1.12	0.70

Assuming $\Delta H_s = 5\times10^{-19}$ J, the proportion of vacant sites n_s/N at 300 K is 6.12×10^{-27}, whereas at 1000 K this increases to 1.37×10^{-8}

At room temperature there are very few Schottky defects, even at 1000K there are only about 1 or 2 defects per hundred million sites.

Depending on the value of ΔH, a Schottky or Frenkel defect may be present. The lower ΔH Frenkel defects dominates, but in some crystals it is possible that both types of defects may be present.

Increasing temperature increase defects.

Extrinsic Defects

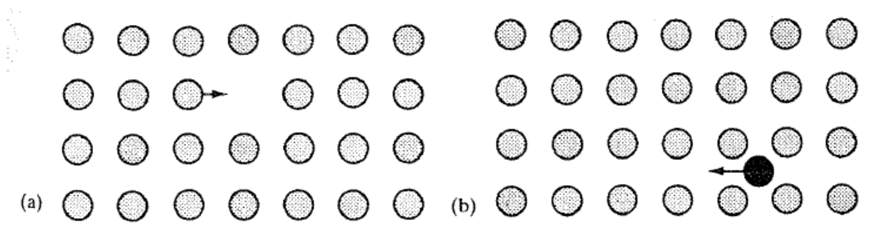
Doping with selected ‘impurities’ can introduce vacancies into a crystal.

Consider incorporating $CaCl_2$ into NaCl, in which each Ca^{2+} replaces one Na^+ and creates one cation vacancy.

Defects and Ionic Conductivity in Solids

Defects make it possible for atoms or ions to move, through diffusion through the lattice or ionic conductivity (ions under the influence of an external electric field) through the structure.

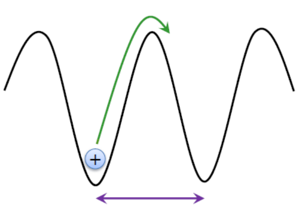
Two possible mechanisms for the movement of ions through a lattice:



Vacancy mechanism Interstitial mechanism

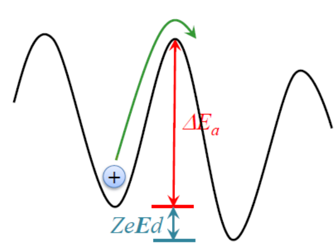
Ionic Conduction: Activation Energy

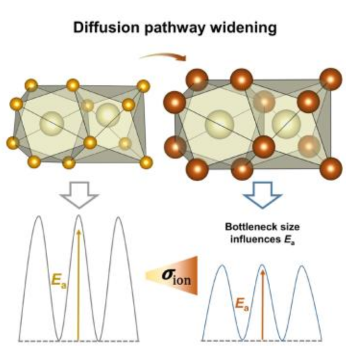
Electric field E = 0



Average spacing between adjacent sites: d

Electric field E > 0





Prog. Energy **2** (2020) 022001

Ionic Conductivity: Arrhenius Equation

The temperature dependence of the mobility of the ions can be expressed by an Arrhenius equation.

$$\mu \propto \exp\left(\frac{-E_a}{kT}\right) \text{ or } \mu = \mu_0 \exp\left(\frac{-E_a}{kT}\right)$$

where μ_o is a proportionality constant known as the pre-exponential factor

μ_o depends on the attempt frequency (frequency of vibration of the lattice 10^{12}-10^{13} Hz), distance moved by ion, and the size of the external field.

If the external field is small (up to 300 V/cm), a temperature dependence of 1/T is present in the pre exponential factor.

An expression for the variation of ionic conductivity: $\sigma = \frac{\sigma_0}{T}\exp\left(-\frac{\Delta E_a}{k_B T}\right)$

The term σ_0 contains n and Zq as well as the attempt frequency and jump distance. Taking logs…

$$\ln \sigma T = \ln \sigma_0 - \left(\frac{E_a}{k_B T}\right)$$

Plotting ln(σT) vs 1/T should produce a straight line with a slope of $-E_a$.
Ln(σ) vs 1/T is also used

Ionic Conductivity in NaCl

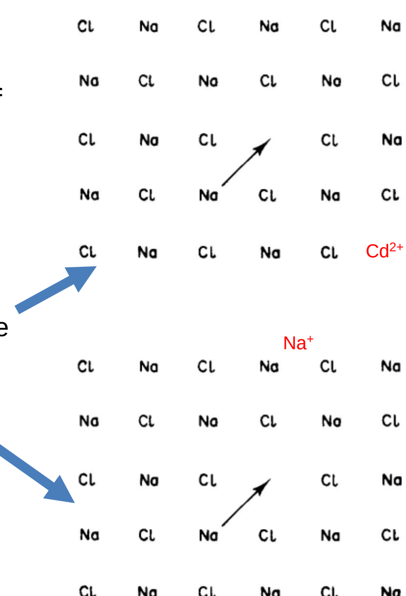
NaCl is a poor ionic conductor

Conduction involves migration of cation vacancies

Cation vacancies are present due to

– doping - extrinsic defects (for example Cd^{2+})

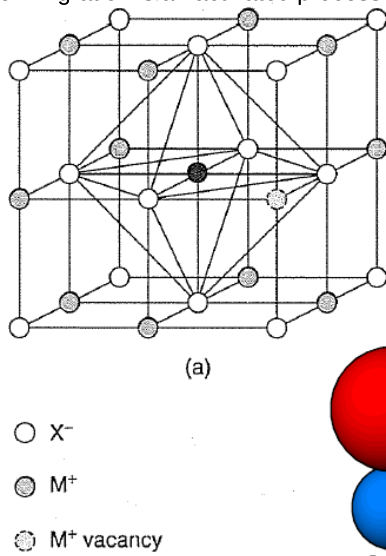
– Schottky defects – intrinsic defects



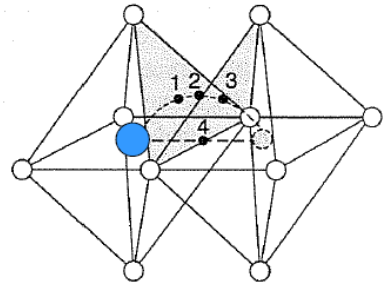
Ion Migration in NaCl: Schottky Defects

Na⁺ ions move, but meet resistance in the crystal structure

Ion migration is an activated process: $\boldsymbol{\mu = \mu_0 \exp(-E_a/kT)}$, Arrhenius equation



(a)



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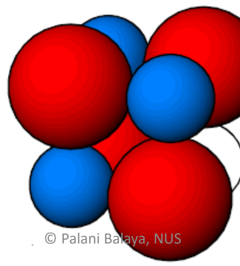
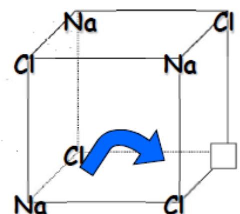




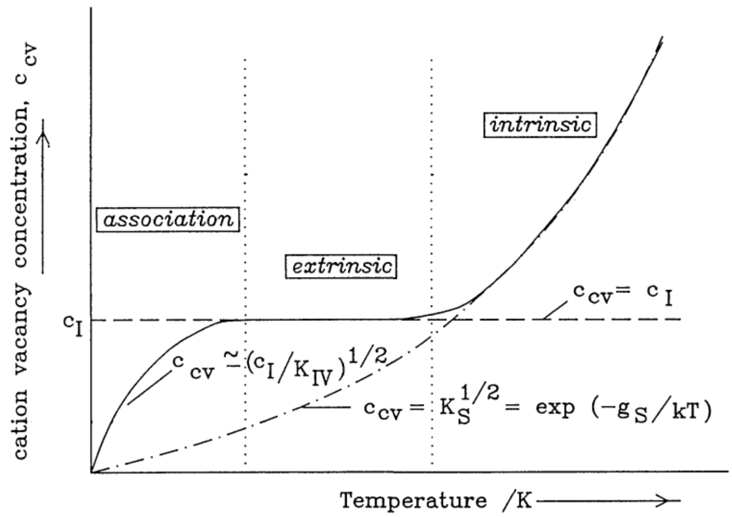
Ion Migration in NaCl: Schottky Defects

For a three-dimensional NaCl lattice, a central cation vacancy can jump to any of the 12 neighboring cation sites, each having a distance $(2a)^{0.5}$ from the vacancy. If the applied field is in (100) or any crystal direction, four possible jumping directions are perpendicular to the field, which will not contribute to the conductivity; four jumping directions are in the direction of the field; and the remaining four are in the direction opposite to the field.

Take this jumping probability into account.

Consider the vacancy is part of the Schottky defect.

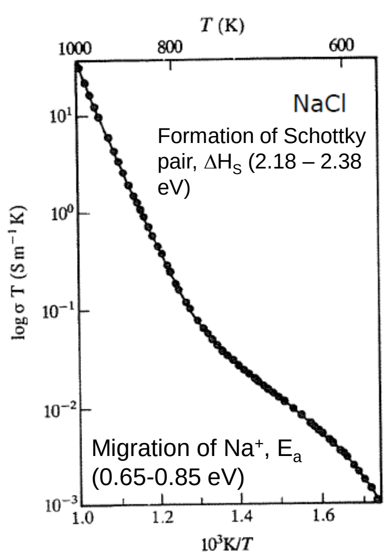
Cation Vacancy Concentration with Temperature



Cation vacancy concentration in a MX crystal with Schottky disorder and doped with a divalent cation as a function of temperature.

Ionic Conduction and Diffusion in Solids, AV Chadwick

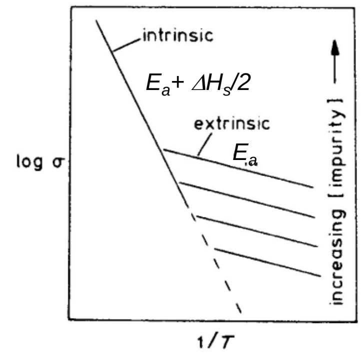
Temperature Dependence of Ionic Conductivity



Idealized Conductivity for NaCl

Differences in slopes are evident, even in very pure crystals.

Low temperature (extrinsic conductivity):



At low temperatures extrinsic vacancies are most important.
The concentration of intrinsic vacancies are so small at low temperature that they may be ignored
The number of vacancies will be essentially constant
μ in the extrinsic region thus will only depend on the cation mobility due to extrinsic defects, with the temperature dependence:

$$\mu = \mu_0 \exp\left(\frac{-E_a}{kT}\right) \qquad \sigma = \frac{\sigma_0}{T}\exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

Carrier concentration is fixed by doping

High Temperature (Intrinsic Conductivity)

At high temperatures the concentration of intrinsic defects has increased so that it is similar or greater than the concentration of extrinsic defects

$$n_s \approx N \exp\left(\frac{-\Delta H_s}{2kT}\right)$$

The conductivity in this intrinsic region on the left side of the plot:

$$\sigma = \frac{\sigma'}{T}\exp\left(\frac{-E_a}{2RT}\right)\exp\left(\frac{\Delta H_s}{2kT}\right)$$

A plot of ln(σT) vs 1/T gives a larger value for the activation energy (E_s), because it depends on both the activation energy for the cation jump (E_a) and the enthalpy of formation of a Schottky defect (ΔH_S).

Slope $E_s = E_a + (1/2)\ \Delta H_S$

<u>For a system with Frenkel defects</u>, slope $E_F = E_a + (1/2)\ \Delta H_F$

Activation energies typically lie in the range of 0.05 to 1.1 eV.

Silver Chloride, AgCl

Defects in AgCl:

The predominant defect in AgCl is cation Frenkel

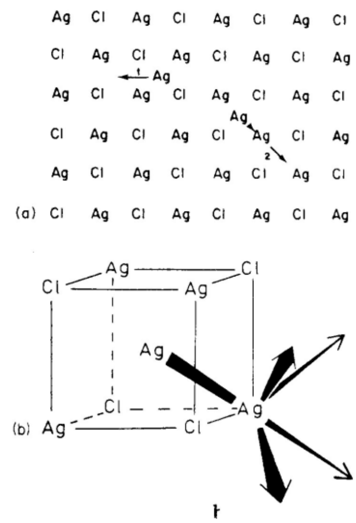
Cation interstitials are more mobile than cation vacancies

Cation interstitials can migrate by one of two mechanisms
– direct movement
– indirect movement

Migration mechanism in AgCl:

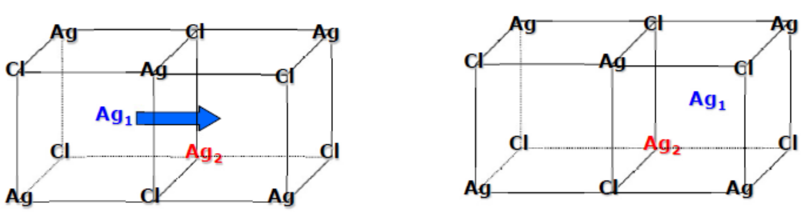
Two possible pathways for interstitial migration:
1) move directly from interstitial to interstitial
2) interstitial displaces regular cation onto interstitial position

Migration actually occurs by second pathway

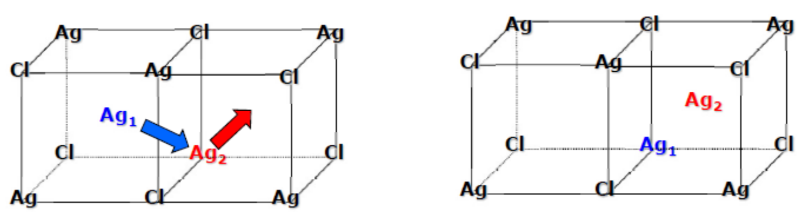


Ion Migration: Frenkel Defects

The Frenkel defects in AgCl can migrate via two mechanisms.



Direct Interstitial Jump



Interstitialcy Mechanism

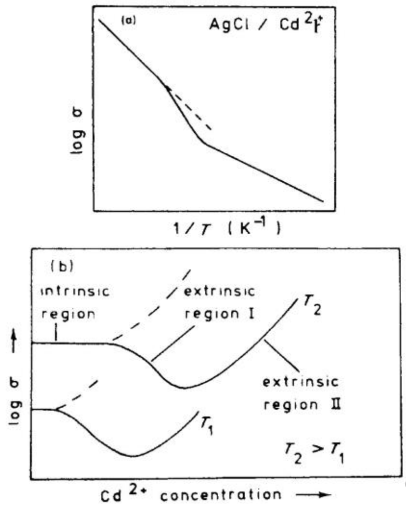
Doping in AgCl

Doping AgCl with a divalent impurity like Cd^{2+} reduces the ionic conductivity of the specimen

There is an equilibrium between cation vacancies and Ag^+ interstitials

– doping increases vacancy concentration

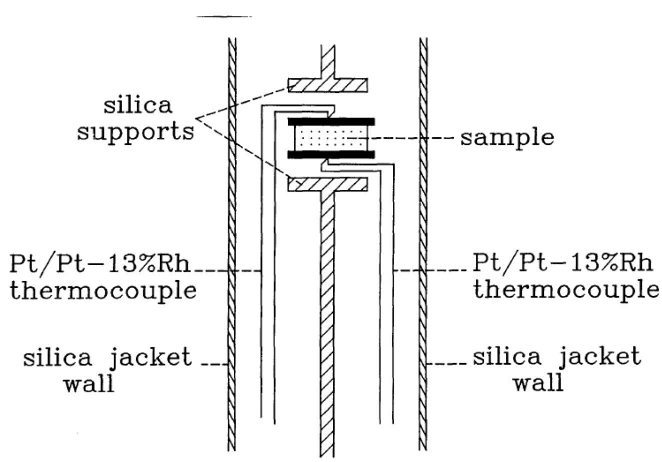
– doping decreases interstitial concentration (Cd^{2+} doped AgCl)



Schematic showing effect of **Cd^{2+}** impurity on conductivity – Presence of **Cd^{2+}** reduces number of Ag^+ interstitials and hence lowers conductivity

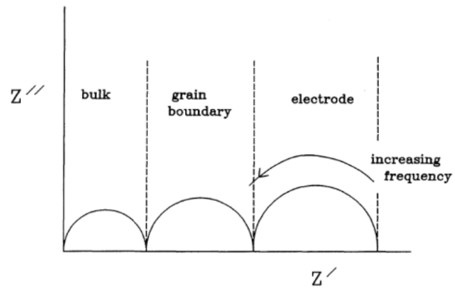
Get minimum in conductivity curve when doped – at high impurity concentrations conductivity is dominated by cation vacancy migration, at low concentrations interstitial migration dominates

Ionic Conductivity - Measurement

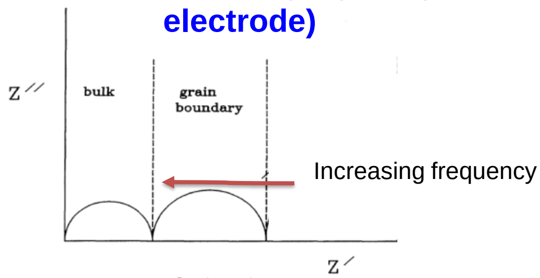


Essential features of a cell for measuring ionic conductivity of solids

Impedance Measurement on Pt/AgCl/Pt (blocking electrode)

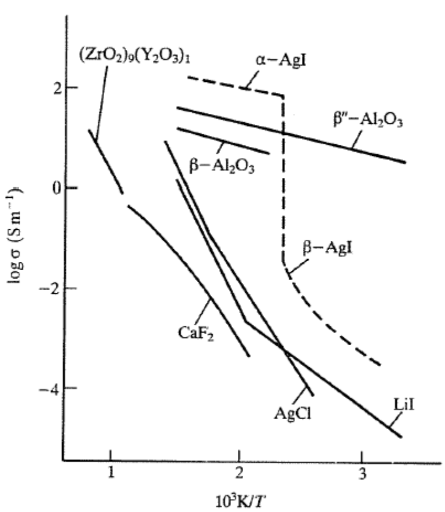


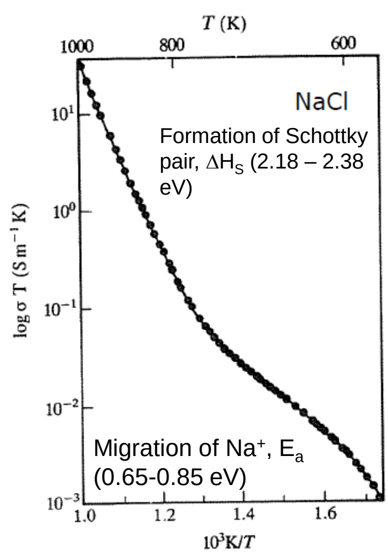
Impedance Measurement on Ag/AgCl/Ag (non-blocking electrode)



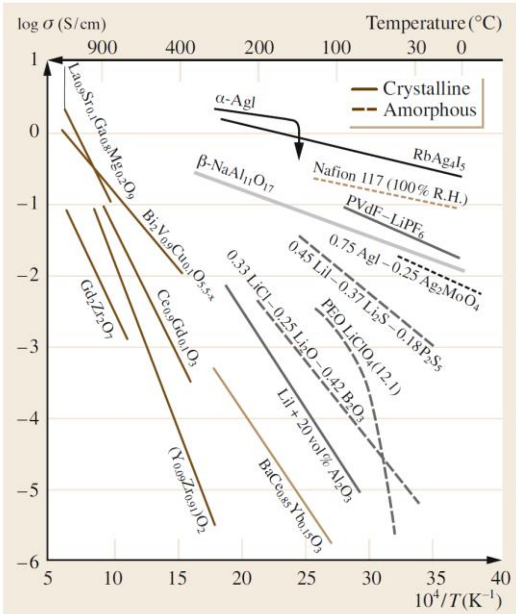
Idealized impedance spectrum of a polycrystalline ionic conductor

Temperature Dependence of Ionic Conductivity





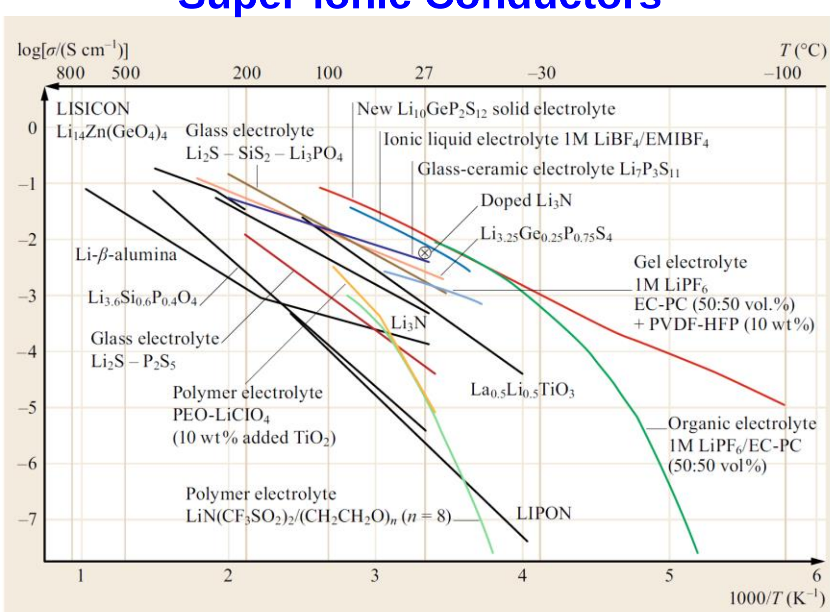
Super-ionic Conductors



The temperature dependences of representative super-ionic conductors, including cation and anion conductors, crystalline and amorphous conductors, and inorganic and organic conductors.

H.L. Tuller: Highly conducting ceramics. In: Ceramic Materials for Electronics, 3rd edn., ed. by R.C. Buchanan (Marcel Dekker, New York 2004), p. 87

Super-ionic Conductors



The temperature dependences solid lithium ion conductors, together with representative organic liquid, ionic liquid and get electrolytes (Nat. Mater. **10**, 682 (2011)

Typical Applications of Ionic and Electronic Conductors

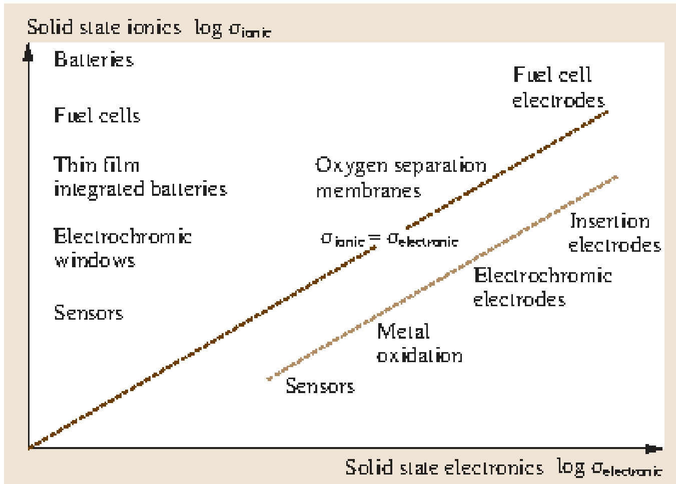


Illustration of typical applications of ionic and electronic conductors as a function of the magnitude of electrical conductivity. Applications requiring mixed ionic electronic conductivity fall within the quadrant bounded by the two axes.

H.L. Tuller: Oxygen ion conduction and structural disorder in conductive oxides, J. Phys. Chem. Solids **55**, 1393 (1994)