INTRODUCTION TO THE DEFECT STATE IN MATERIALS

- **DEFECTS, DEFECTS, DEFECTS**
- ***CAN'T LIVE WITH THEM !!!***
- ***CAN'T LIVE WITHOUT THEM !!!***

INTRODUCTION TO DEFECT STATE IN MATERIALS

- **DEFECTS, DEFECTS, DEFECTS**

- **Perfect crystals**
- **Is there such a thing?**
- **All atoms on correct lattice positions**
- **Can only exist at 0^{o}K**
- **Above 0^{o}K, defects exist in structure**
- **Distinct kinds of defects**

INTRODUCTION TO DEFECT STATE IN MATERIALS

- DEFECTS, DEFECTS, DEFECTS

- Different size and dimensionality
- Intrinsic
- Extrinsic
- Range of concentrations
- Random or ordered
- Isolated or clustered
- Surface and bulk

INTRODUCTION TO DEFECT STATE IN MATERIALS

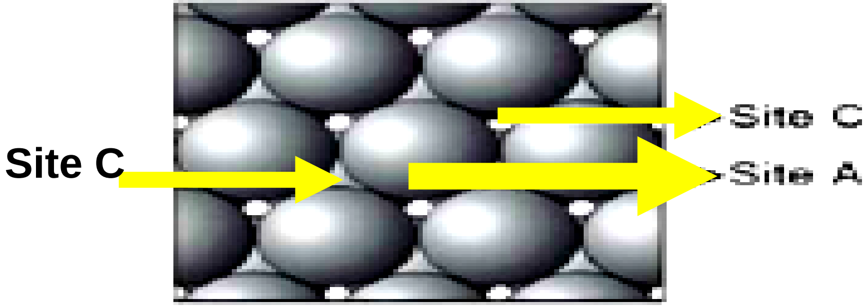
- DEFECTS, DEFECTS, DEFECTS

- Point
- Line
- Plane
- Three dimensional
- Defects clusters, ordered, random
- Grain boundaries between materials

INTRODUCTION TO DEFECT STATE IN MATERIALS

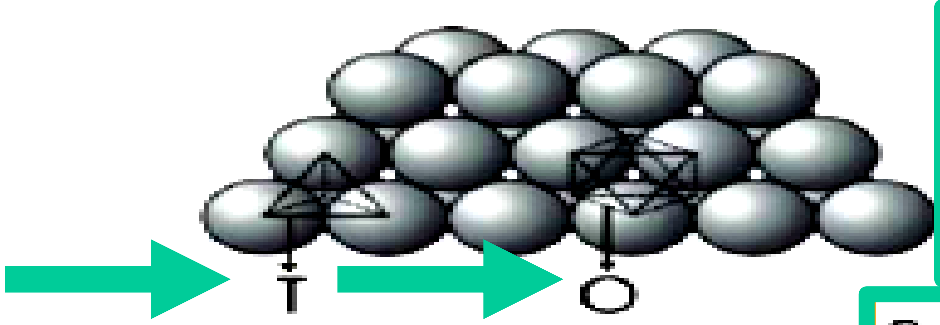
- DEFECTS, DEFECTS, DEFECTS
- Defects control the properties of ***ALL*** solid state materials
- Thermodynamics of defect formation
- Defect control of Charge Transport, Optical, Magnetic and Mechanical Properties, Chemical Reactivity, Crystal Nucleation and Growth, Superconductivity

Close packed structures of spheres



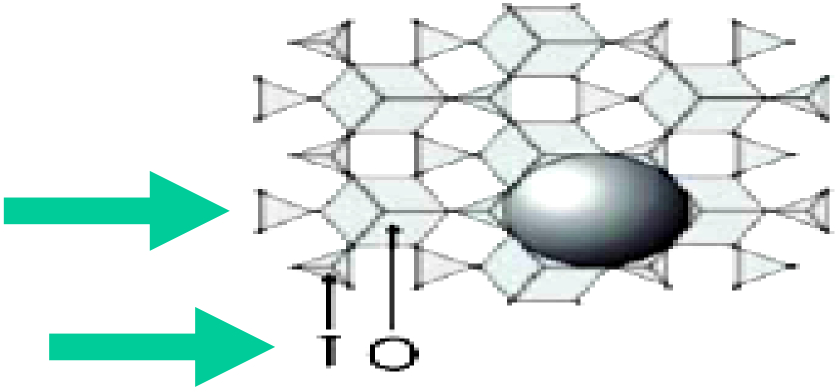
Face centered cubic (FCC) or cubic close packed (CCP): ABCABC.....

hexagonal close packed (HCP): ABABAB.....



N spheres
N octahedral holes
2N tetrahedral holes

Octahedral hole: Coordination 6
Tetrahedral hole: Coordination 4



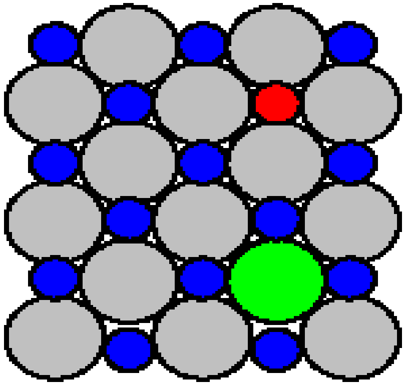
Rock salt (NaCl) structure: CCP array of N anions, N cations occupying all the octahedral holes.

Fluorite structure (CaF_2): CCP array of N cations, 2N anions occupying all the tretrahedral holes.

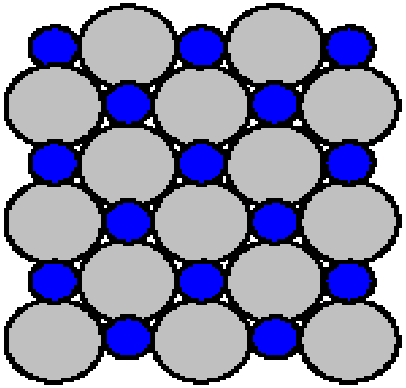
Zinc blende structure (ZnS(c)): CCP array of N atoms of type A, N atoms of type B occupying every other tetrahedral hole.

Wurtzite structure (ZnS(h)): HCP array of N atoms of type A, N atoms of type B occupying every other tetrahedral hole.

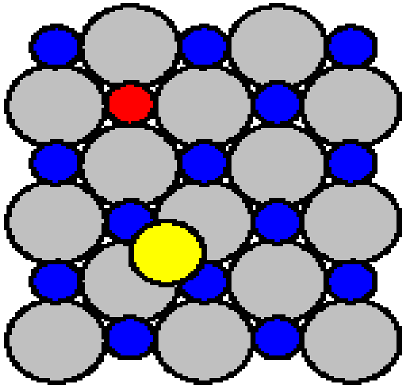
INTRINSIC POINT DEFECTS



Schottky Pair
Cation-anion
vacancy



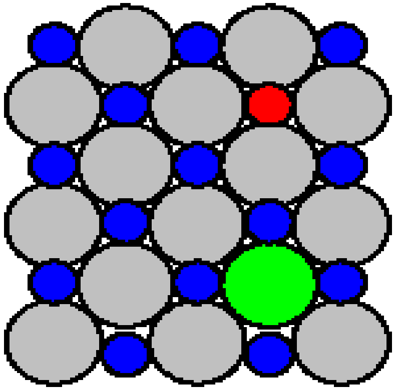
Perfect
Crystal



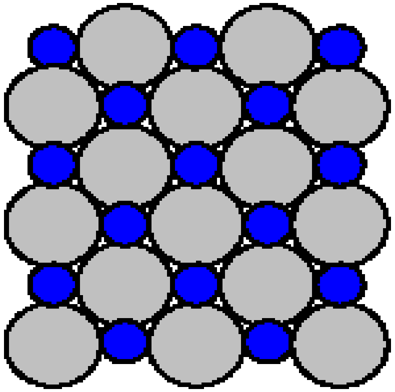
Frenkel Pair
Cation vacancy,
interstitial cation

- Schottky defect: substitutional vacancies
- Schottky pairs
- Cation-anion pair with charge balance
- Requires electroneutrality of lattice
- MX 1 : 1 for M^+ and X^-
- MX_2 1 : 2 for M^{2+} and $2X^-$

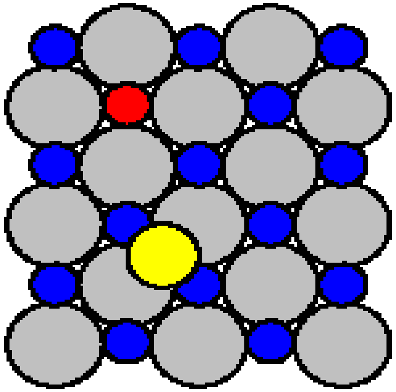
INTRINSIC POINT DEFECTS



Schottky Pair
Cation-anion
vacancy



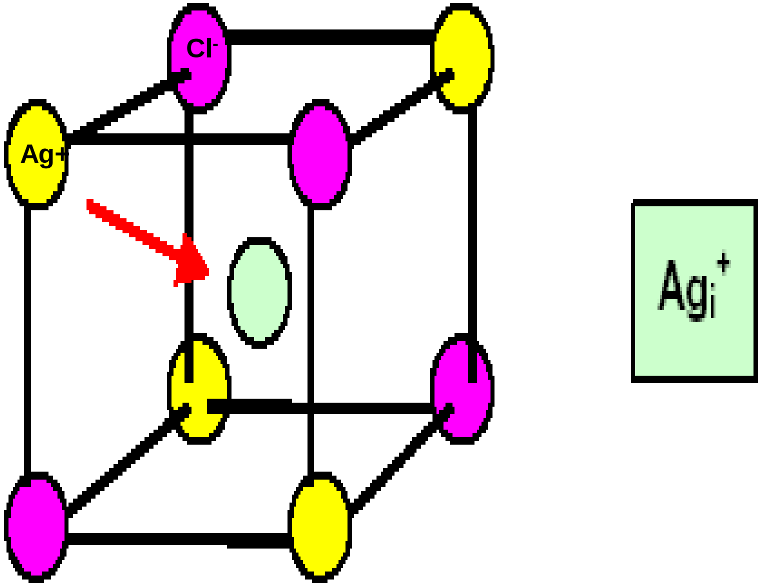
Perfect
Crystal



Frenkel Pair
Cation vacancy,
interstitial cation

- **Frenkel defect: interstitial ion - ion vacancy pair**
- **Ion moves from substitutional into interstitial position**
- **Usually smaller cation e.g., rock salt structure AgCl, where Ag^+ moves into spacious interstitial site of larger Cl^- anion sub-lattice**
- **Reverse case for fluorite structure, MF_2, MO_2**
- **Smaller F^-/O^{2-} anion moves into interstitials of larger M^{2+} cation sub-lattice**

COORDINATION OF FRENKEL CATIONS AND ANIONS



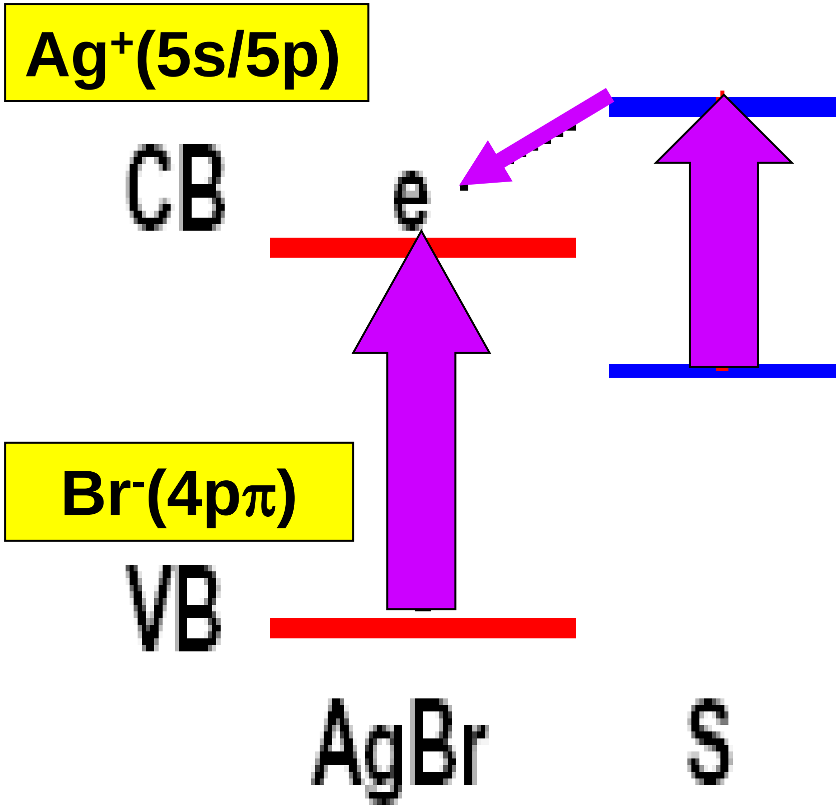
- **Cationic Frenkel’s**

- **In rock salt AgCl**

- **Ag$^+$ moves from Oh substitutional sites to Td interstitial sites**

- **Important defect in the silver halide photographic process**

SILVER HALIDE PHOTOGRAPHY

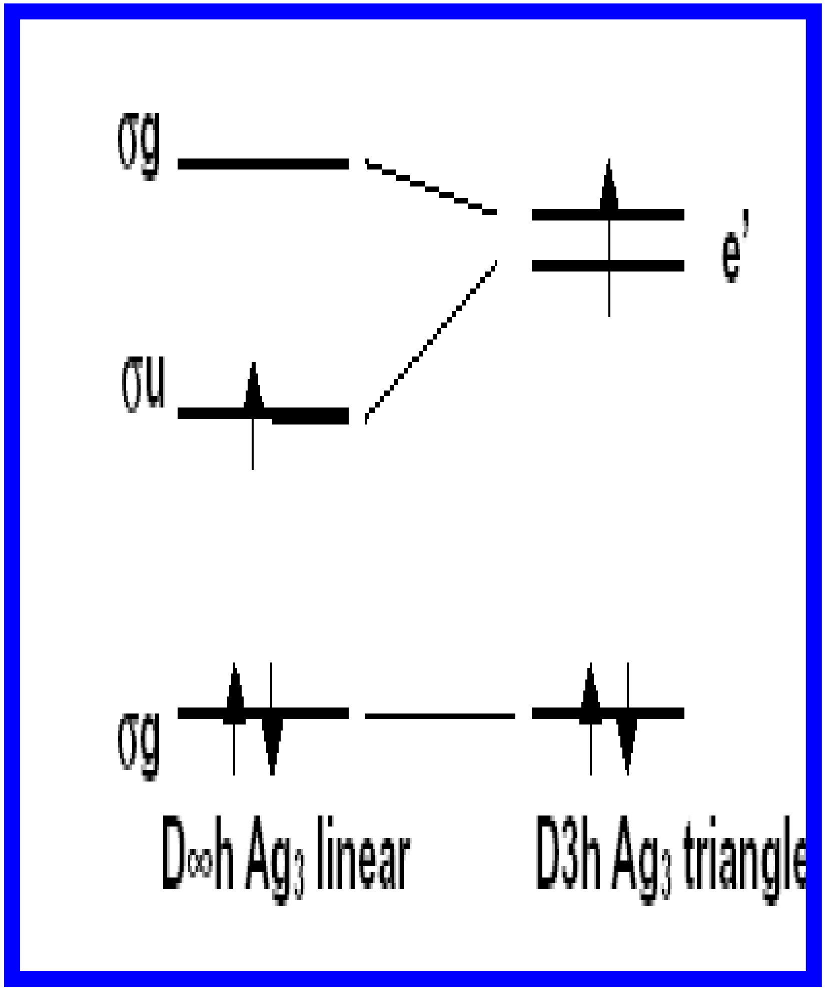


- Photographic emulsion, AgBr/sensitizer/gelatin/ plastic film
- 0.05-2.0 μm size AgBr grains
- VB to CB e-h excitation in grain (Eg = 2.7 eV)
- Simultaneous sensitizer S e-h excitiation (dye molecule) extends range of absorption across visible

FORMING THE PHOTOGRAPHIC LATENT IMAGE

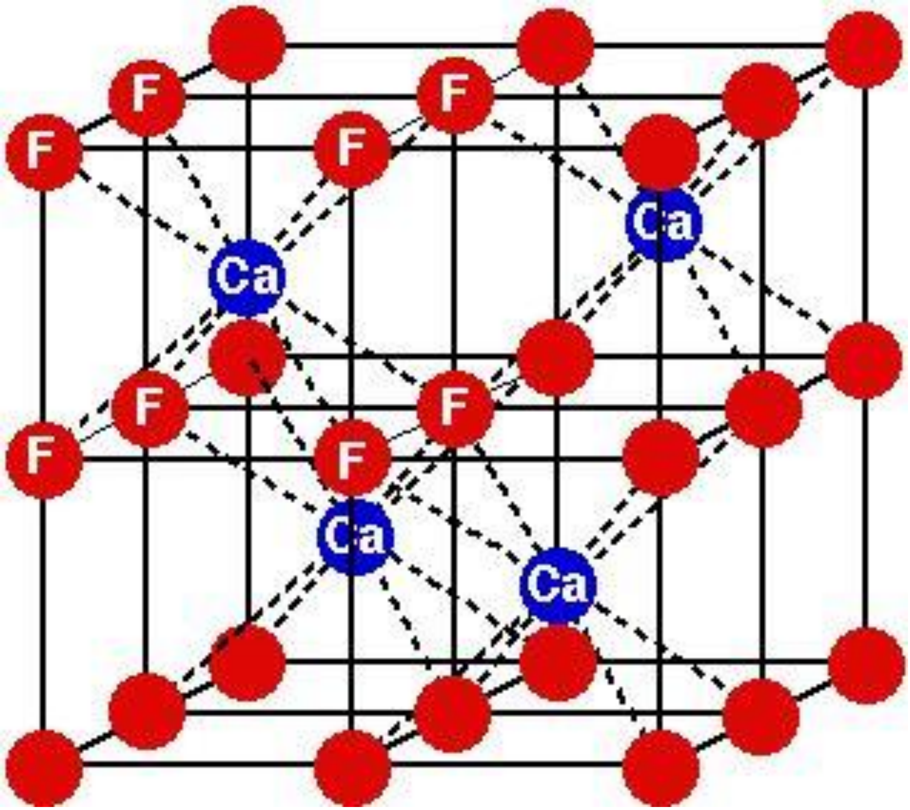
- **Photoelectron trapped on Ag_i^+ gives neutral Ag^0_i in grain**
- **Ag^0_i diffuses and grows by accretion of electrons/ions to give small silver clusters**
- **This is the latent image**
- **Silver clusters in exposed regions developed (further reduced and grown) in hydroquinone (HOC_6H_4OH) HQ RA,**
- **Unreduced Ag^+ in unexposed regions washed away with sodium thiosulfate $Na_2S_2O_3$**
- **Forms soluble silver thiosulfate complexes $[Ag(S_2O_3)_2]^{3-}$**

FORMING THE PHOTOGRAPHIC LATENT IMAGE



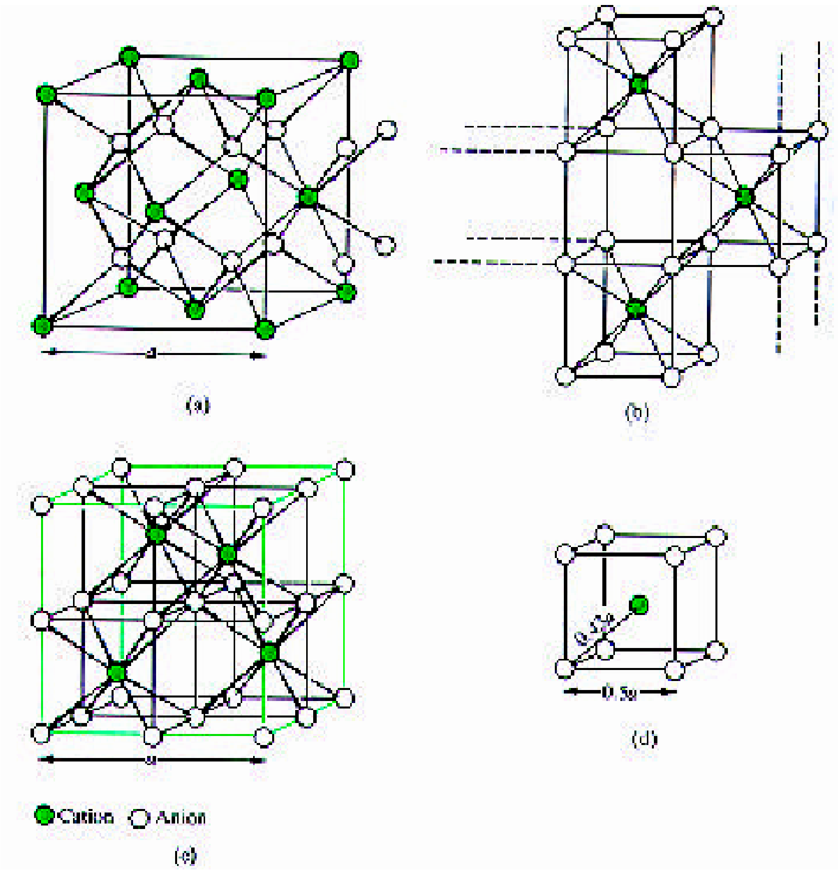
- $Ag_i^+ + e = Ag^0$
- $Ag^0 + e = Ag^-$
- $Ag^- + Ag_i^+ = Ag^0_2$
- $Ag^0_2 + Ag_i^+ = Ag_3^+$
- $Ag_3^+ + e = Ag^0_3$
- $Ag^0_3 + e = Ag_3^-$
- $Ag_3^- + Ag_i^+ = Ag^0_4$
- “Latent image” thought to be a silver cluster of nuclearity 2-4 developed and grown to micron size silver grain
- Notable 10^{21} TOs/hν

Archetype Fluorite CaF_2 Lattice



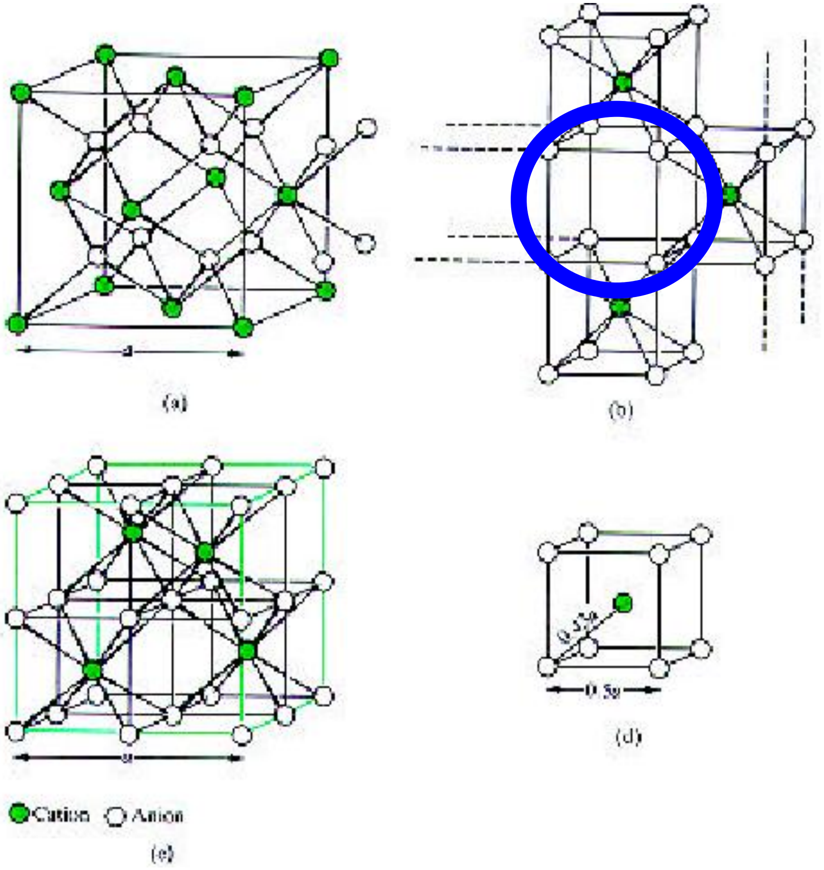
- Cations occupy half of the octant cubes in fcc anion lattice
- Lots of interstitial space in which the smaller anions can move

COORDINATION OF FRENKEL CATIONS AND ANIONS



- **Anionic Frenkel's**
- **Fluorite lattice**
- **ccp M^{2+} or M^{4+}**
- **O^{2-} or F^{-} in all Td sites**
- **SrF_2, PbF_2, UO_2, ZrO_2**
- **O^{2-} much lower charge than M^{4+}**
- **F^{-} lower charge than M^{2+}**
- **Small anions in large cation lattice**
- **Inter-anion repulsions also favor anion mobility**

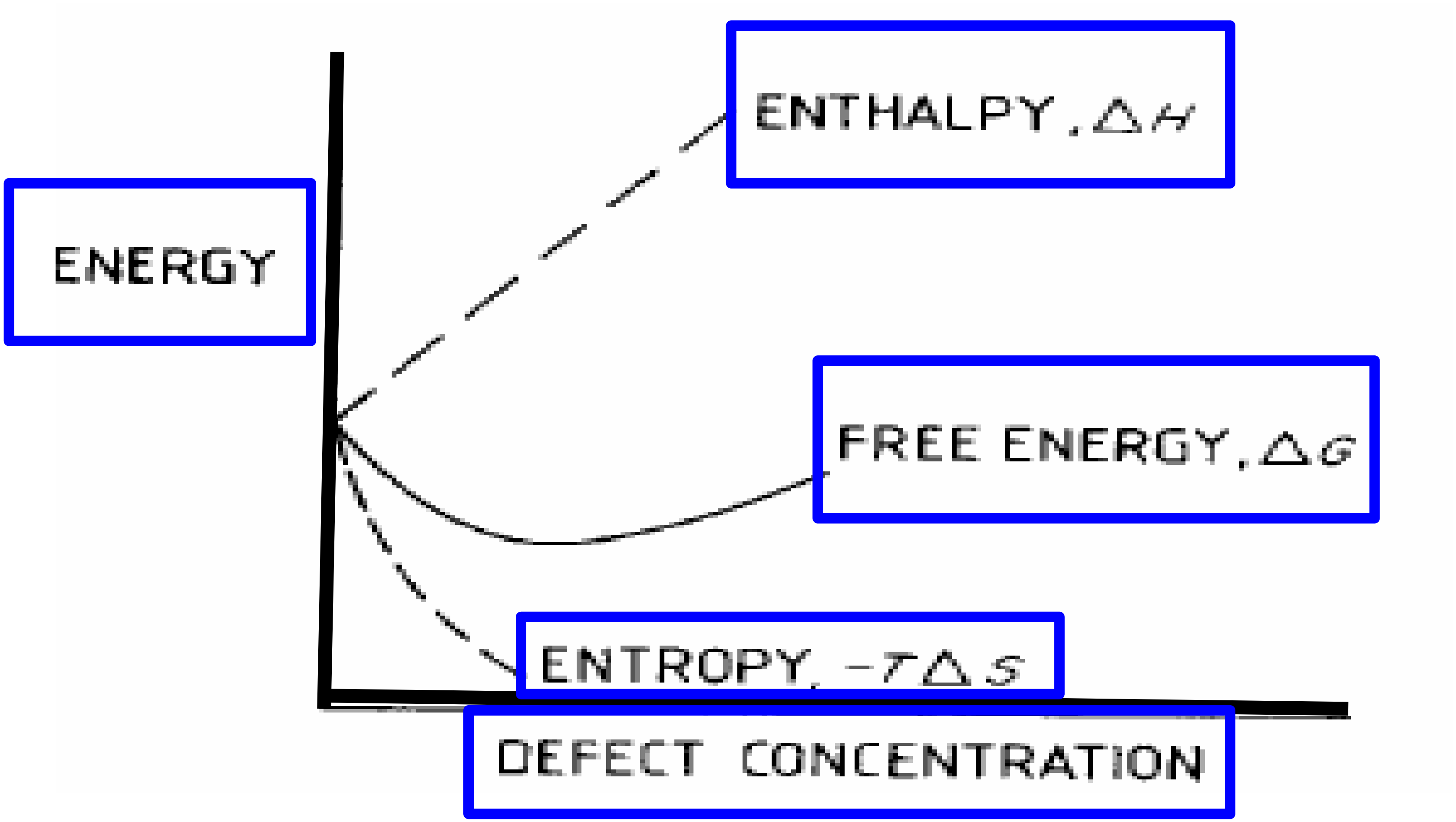
COORDINATION OF FRENKEL CATIONS AND ANIONS



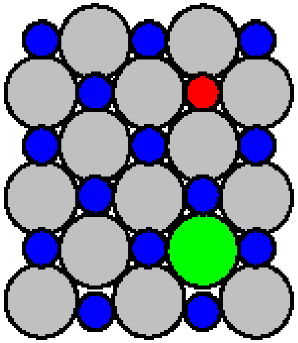
- Very open structure for O^{2-} and F^-
- Cations occupy alternate (half) MO_8/MF_8 anionic octant cubes
- Lots of interstitial octant empty sites for transport of small interstitial Frenkel O^{2-} or F^-
- Optimum situation for ionic mobility via diffusion of interstitial anions

Thermodynamics of Defect Formation

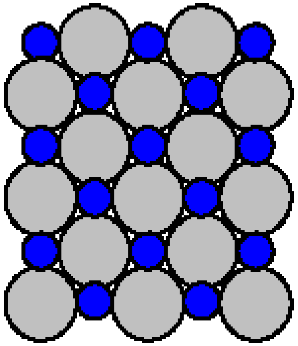
Balance of Entropic Advantage over Enthalpic Demand



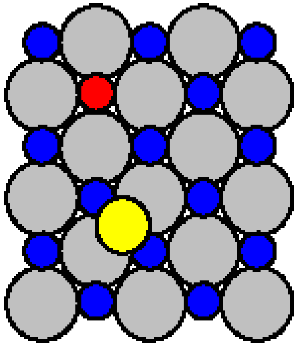
THINKING DEEPER ABOUT INTRINSIC POINT DEFECTS



Schottky Pair
Cation-anion
vacancy



Perfect
Crystal



Frenkel Pair
Cation vacancy,
interstitial cation

- **Define ΔH_S and ΔH_F as enthalpy to form one Schottky and one Frenkel defect respectively**
- **Change kT to RT for one mole of defects**
- **N available substitutional and N_i interstitial lattice sites**

CONCENTRATION OF INTRINSIC DEFECTS

- Energy to form a defect involves movement out of lattice site and is always endothermic and must relate to lattice energy and hence size and charge on constituent ions
- Defect formation involves large configurational entropy driving force (increase in degree of disorder of lattice)
- $\Delta G = \Delta H - T\Delta S$
- Calculation of free energy provides equilibrium concentration of defects

CONCENTRATION OF INTRINSIC DEFECTS

- $S = k \ln W$
- Boltzmann formula for configurational entropy gives total number of ways of distributing n_s cation and n_s anion vacancy defects per unit volume randomly over N lattice sites
- $W_C = N!/(N - n_s)!n_s!$
- $W_A = N!/(N - n_s)!n_s!$
- $W = W_C W_A$

CONCENTRATION OF INTRINSIC DEFECTS

- $\Delta S = 2k\ln [N!/(N - n_s)!n_s!]$
- Stirling's approximation for large N
- $\ln N! \sim N\ln N - N$
- $\Delta S = 2k\{N\ln N - (N - n_s)\ln(N - n_s) - n_s\ln n_s\}$

CONCENTRATION OF INTRINSIC DEFECTS

- $\Delta G = n_s \Delta H_s - 2kT\{N\ln N - (N - n_s)\ln(N - n_s) - n_s \ln n_s\}$

- $(d\Delta G/dn_s) = 0$ at equilibrium

- Notes: NlnN is constant differential zero
- And differential lnx = 1/x and xlnx = 1+lnx and $N \gg n_s$

- $\Delta H_s = 2kT\ln[(N - n_s)/n_s]$

CONCENTRATION OF INTRINSIC DEFECTS

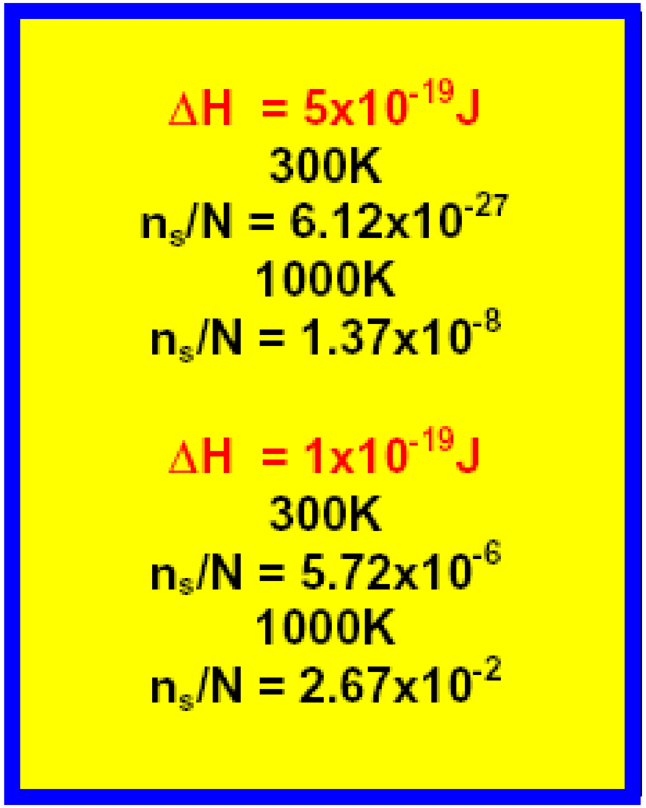
- $\Delta H_s = 2kT\ln[(N - n_s)/n_s]$
- $n_s = N\exp(-\Delta H_s/2kT)$
- Similar arguments for number of Frenkel's n_F per unit volume where N_i is number of interstitial sites available and N is number of substitutional lattice sites
- $n_F = (NN_i)^{1/2}\exp(-\Delta H_F/2kT)$

ENTHALPY OF FORMATION OF INTRINSIC SCHOTTKY AND FRENKEL DEFECTS

defect type	compound	ΔH (10^{-19}J)	ΔH (eV)
Schottky	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	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
	beta-AgI	1.12	0.70

Enthalpy of formation scale with lattice energy and size of sites
Controlled by electrostatic interactions

ENTHALPY OF FORMATION OF INTRINSIC SCHOTTKY AND FRENKEL DEFECTS



$\Delta H = 5\times10^{-19}$J

300K

$n_s/N = 6.12\times10^{-27}$

1000K

$n_s/N = 1.37\times10^{-8}$

$\Delta H = 1\times10^{-19}$J

300K

$n_s/N = 5.72\times10^{-6}$

1000K

$n_s/N = 2.67\times10^{-2}$

- **Whether Schottky or Frenkel defects found depends on the lower value of the enthalpy of formation**
- **The concentration of defects depends sensitively on the temperature, pressure, structure, dopants, impurities, non-stoichiometry**

EXTRINSIC DEFECTS

- Intrinsic Schottky and Frenkel point defects thermodynamically favored by configurational entropy
- Number depends on enthalpy of formation and temperature
- Extrinsic defects can be introduced intentionally by doping with a higher/lower valency cation or anion (aliovalent) or through the presence of non-stoichiometry (AB_{1-x}) or adventitiously from impurities

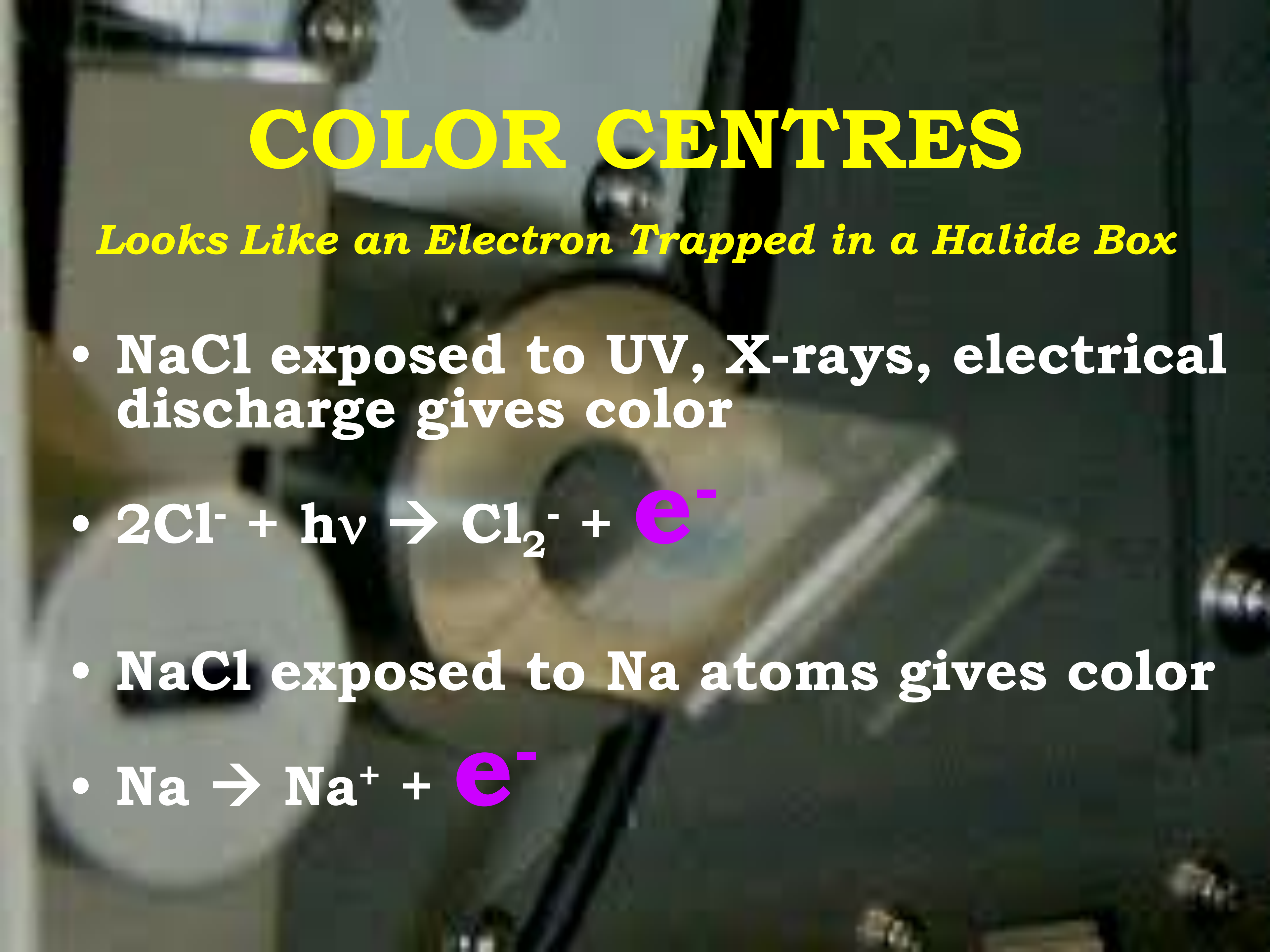
ALIOVALENT EXTRINSIC DEFECTS

- Adding $CaCl_2$ to NaCl
- Preserving electroneutrality
- One Ca^{2+} replaces two Na^+
- $Ca_xNa_{1-2x}Cl$
- Creates one cation vacancy – enables Na^+ mobility

- Adding Ag_2S to AgCl
- Preserving electroneutrality
- One S^{2-} replaces two Cl^-
- AgS_xCl_{1-2x}
- Creates one anion vacancy – enables Cl^- mobility

EXTRINSIC DEFECTS

- Clearly **fraction** of extrinsic dopant determines concentration of vacancies
- Adding CaO to Fluorite type ZrO_2 creates O^{2-} substitutional vacancies and facilitates oxide ion conductivity
- Useful for design of chemical sensor and fuel cell materials – e.g. calcium stabilized zirconia which require O^{2-} ion conductivity
- *e.g.* $Ca_xZr_{1-x}O_{2-x}$

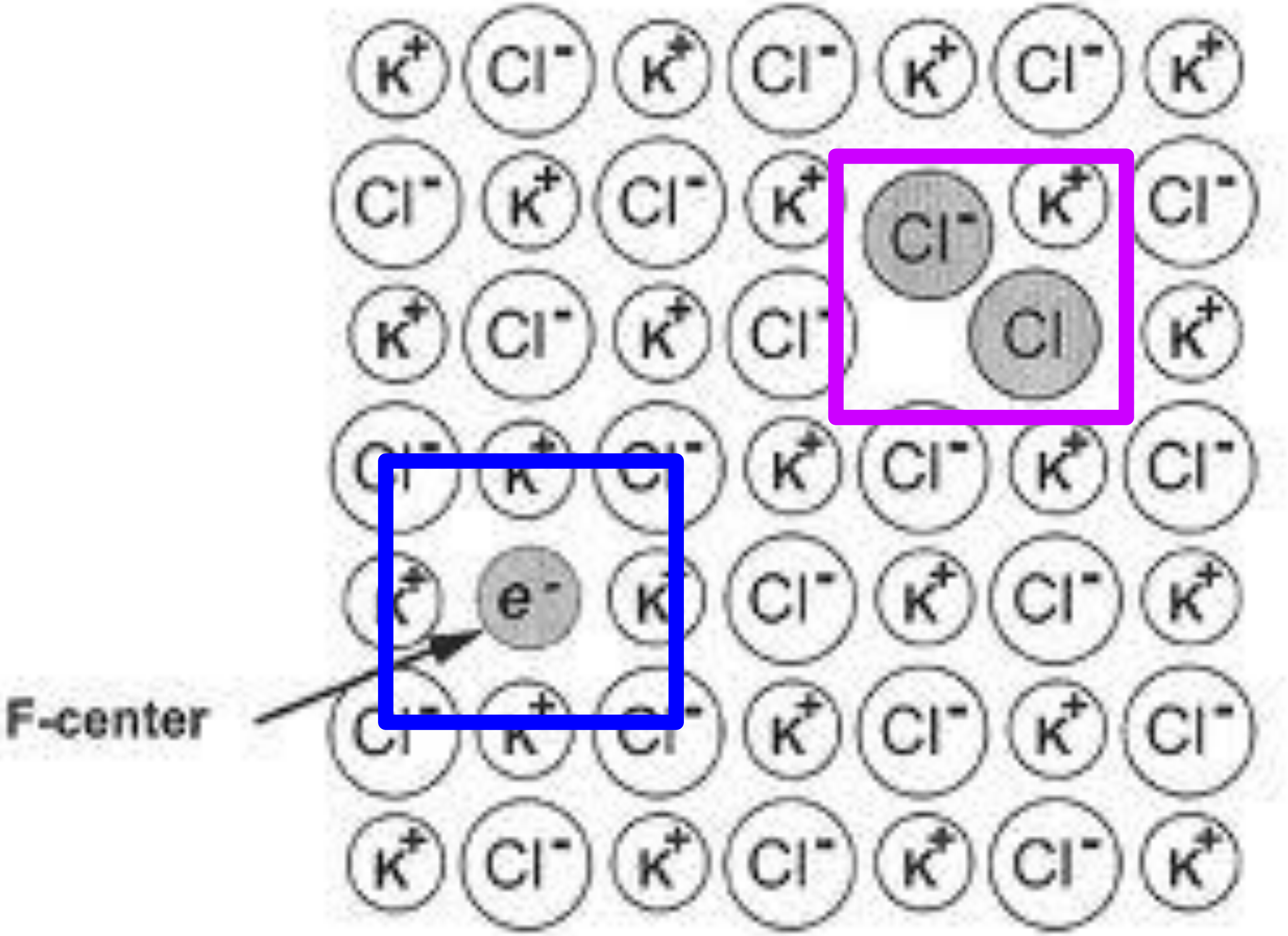


COLOR CENTRES

Looks Like an Electron Trapped in a Halide Box

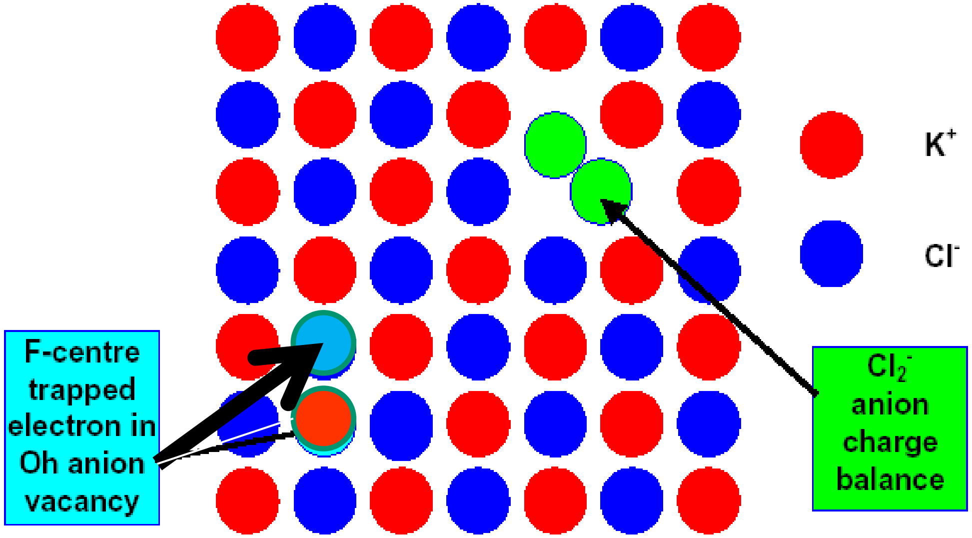
- NaCl exposed to UV, X-rays, electrical discharge gives color
- $2Cl^- + h\nu \rightarrow Cl_2^- + e^-$
- NaCl exposed to Na atoms gives color
- $Na \rightarrow Na^+ + e^-$

F-Center



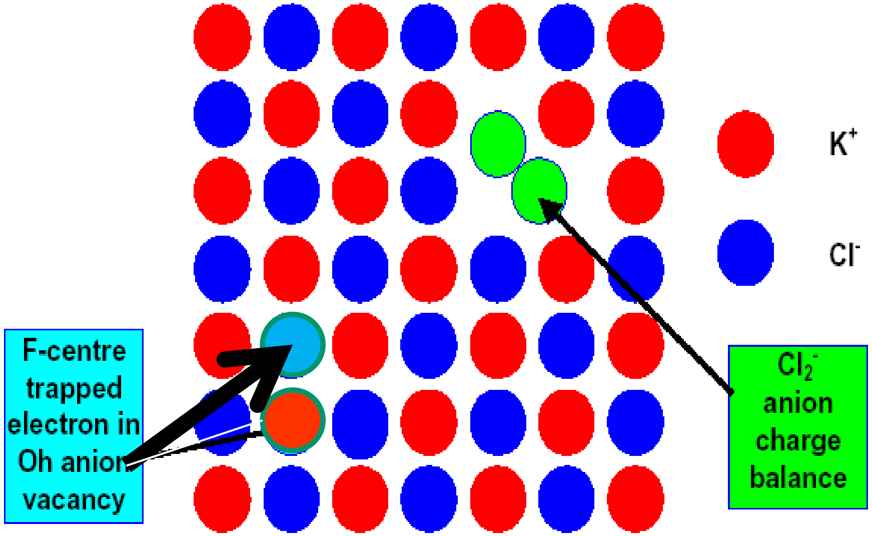
COLOR CENTRES

Looks Like an Electron Trapped in a Halide Box



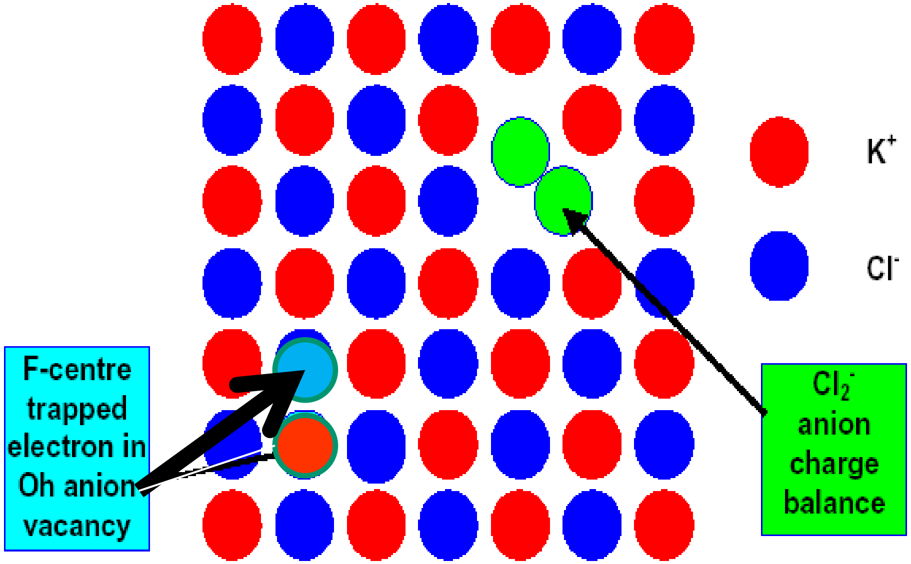
- Rock salt exposed to UV, X-rays, electrical discharge ($2Cl^- + h\nu \rightarrow Cl_2^- + e^-$)
- As well as alkali atoms ($Na \rightarrow Na^+ + e^-$)
- Become brightly colored
- Schottky defects favored in rock salt
- Known as a Farbenzentre
- Called an F-centre, or color centre
- Basis of F-center laser

COLOR CENTRES



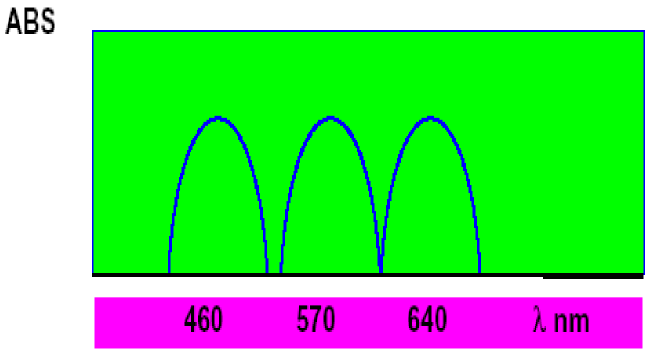
- Color characteristic of host rock salt crystal
- Red shifts with anion size
- Does not shift if Na or K added to NaCl (cation + electron in anion vacancy)
- Electron Spin Resonance ESR spectroscopy shows electron coupling with six cations
- Electron trapped in Oh anion site in rock salt lattice

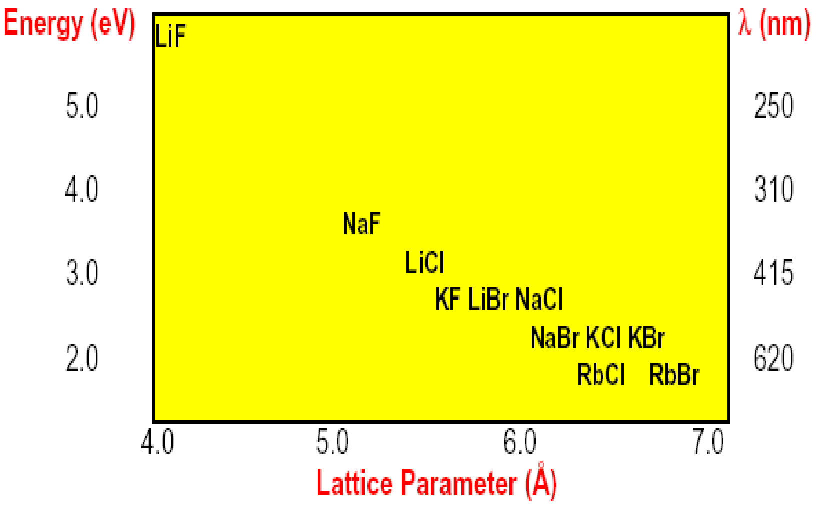
COLOR CENTRES



- Defines electron trapped in substitutional anion vacancy surrounded by six cation lattice site
- Number of F-centres ~ 1 in 10,000 halide ions
- Charge-balance achieved with H-centre Cl_2^- trapped in halide vacancy for UV or X-ray excitation

SPECTROSCOPY OF F-CENTRES
ELECTRON IN A BOX MODEL

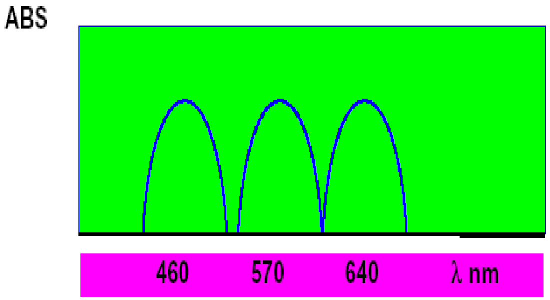


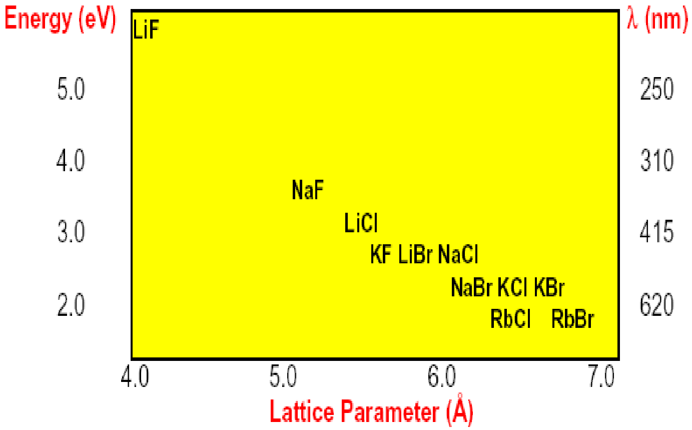


- Broad absorptions traversing UV (LiF) to near IR (RbBr)
- Absorptions shift red with the size of the halide
- Plot of F-centre absorption energy vs a which is the size of the box (anion trapping site)

- $E \sim a^{-1.8}$

SPECTROSCOPY OF F-CENTRES
ELECTRON IN A BOX MODEL

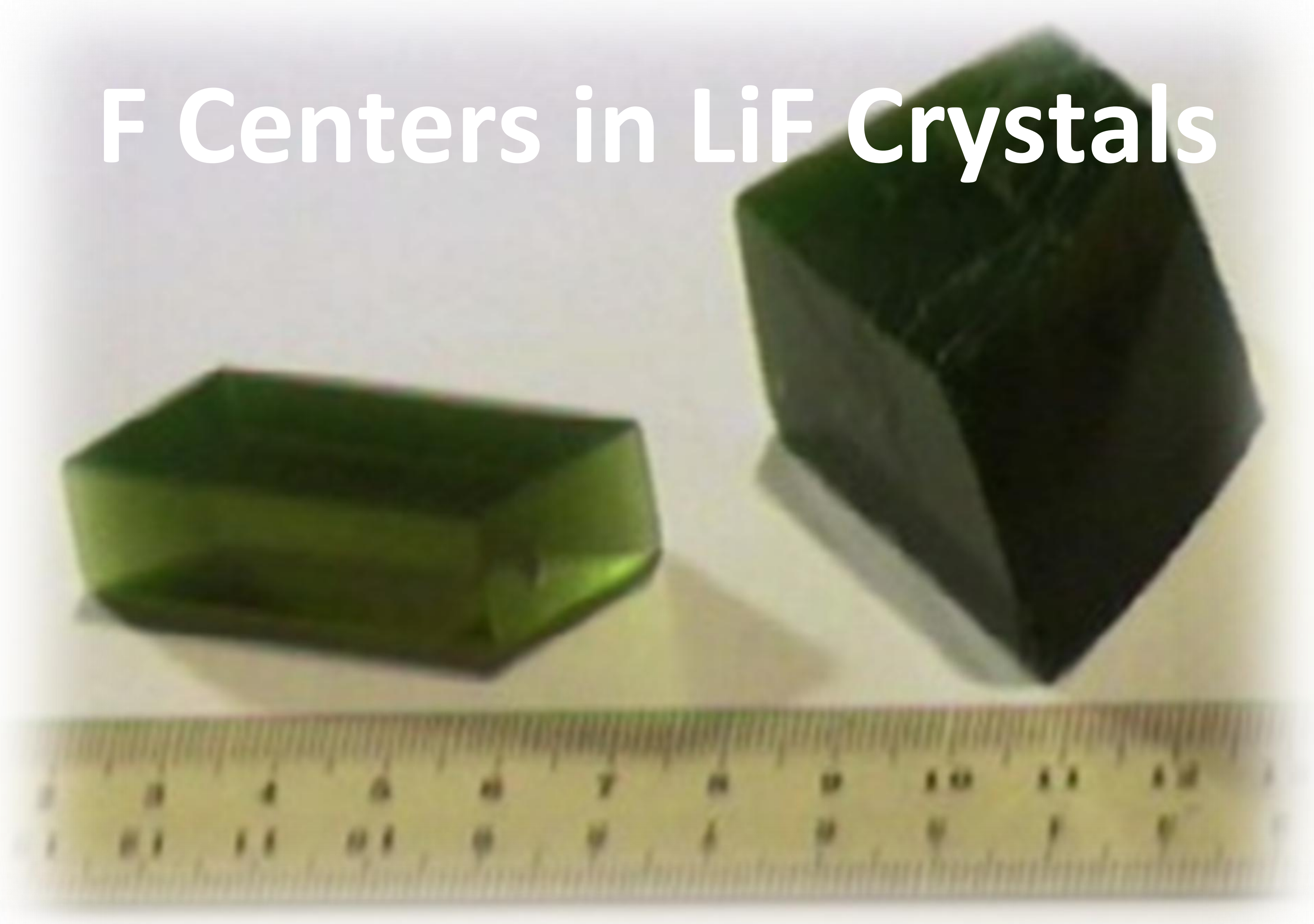




- **Roughly modeled as an electron in a cubic box**
- **Pressure causes box to shrink and absorption to blue shift to higher energy**
- **Reduced temperature has a similar effect – lattice contraction, smaller amplitude of lattice vibrations (phonons) – high energy blue color shift**

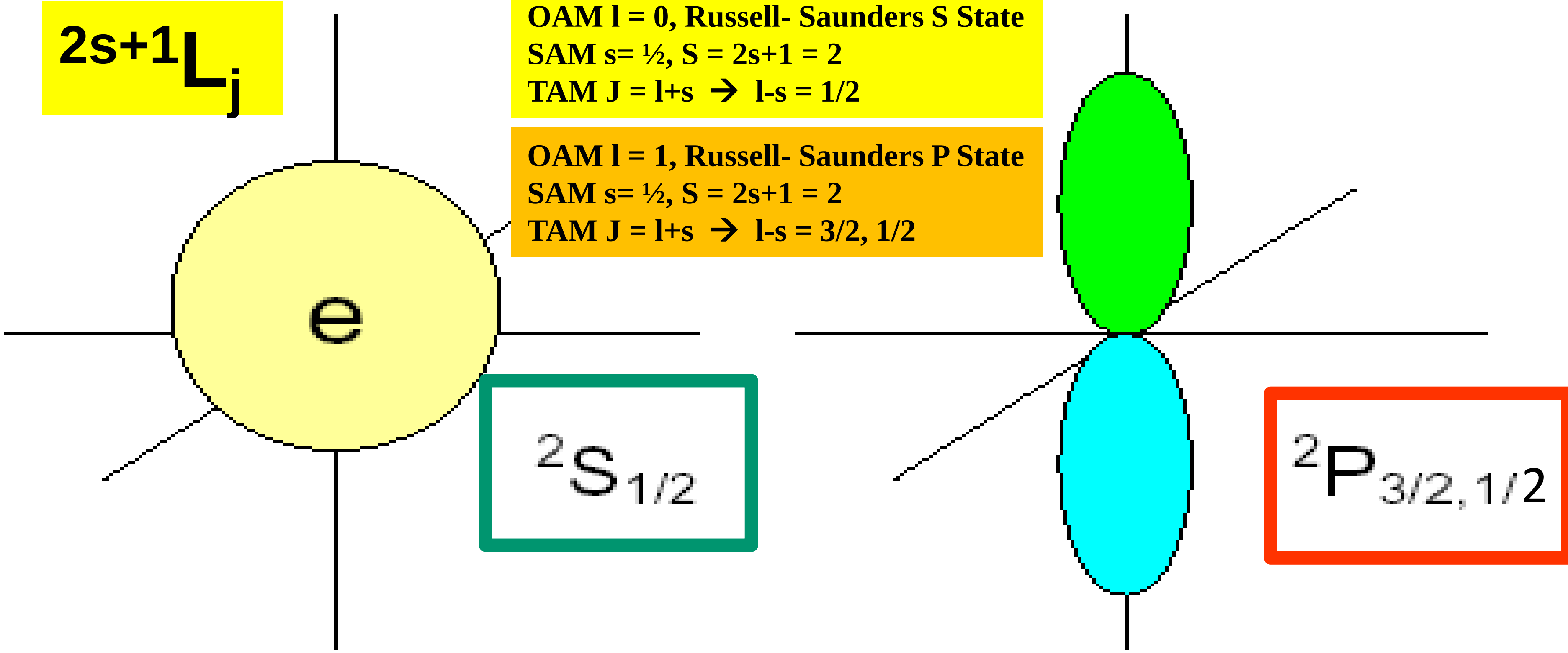
How would you make an F-Centre laser from a grain of salt ???

F Centers in LiF Crystals



Origin of F-Center Color

Electron Trapped in Halide Box – Spectroscopic States



$^{2s+1}L_j$

OAM l = 0, Russell- Saunders S State
SAM s= ½, S = 2s+1 = 2
TAM J = l+s → l-s = 1/2

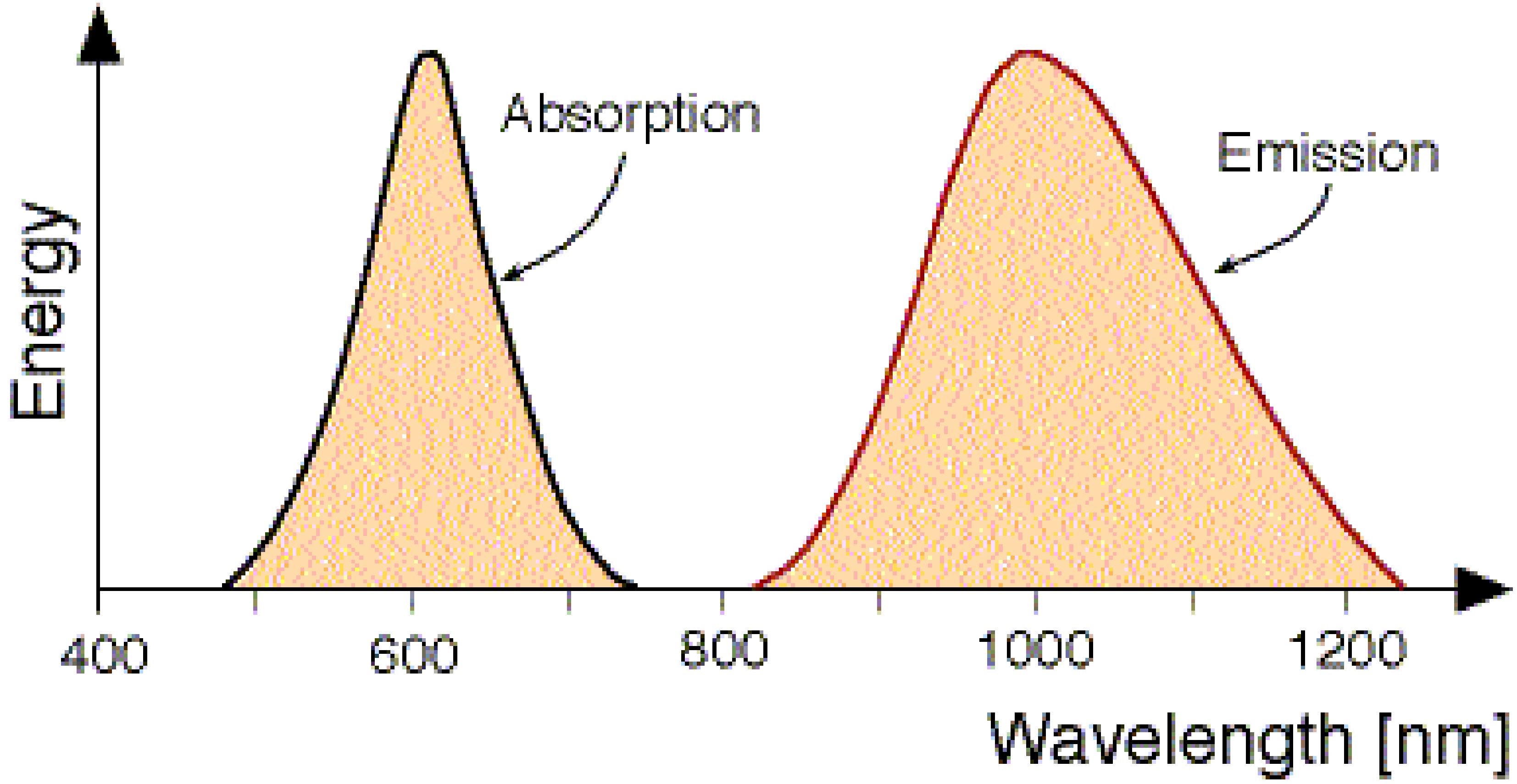
OAM l = 1, Russell- Saunders P State
SAM s= ½, S = 2s+1 = 2
TAM J = l+s → l-s = 3/2, 1/2

$^2S_{1/2}$

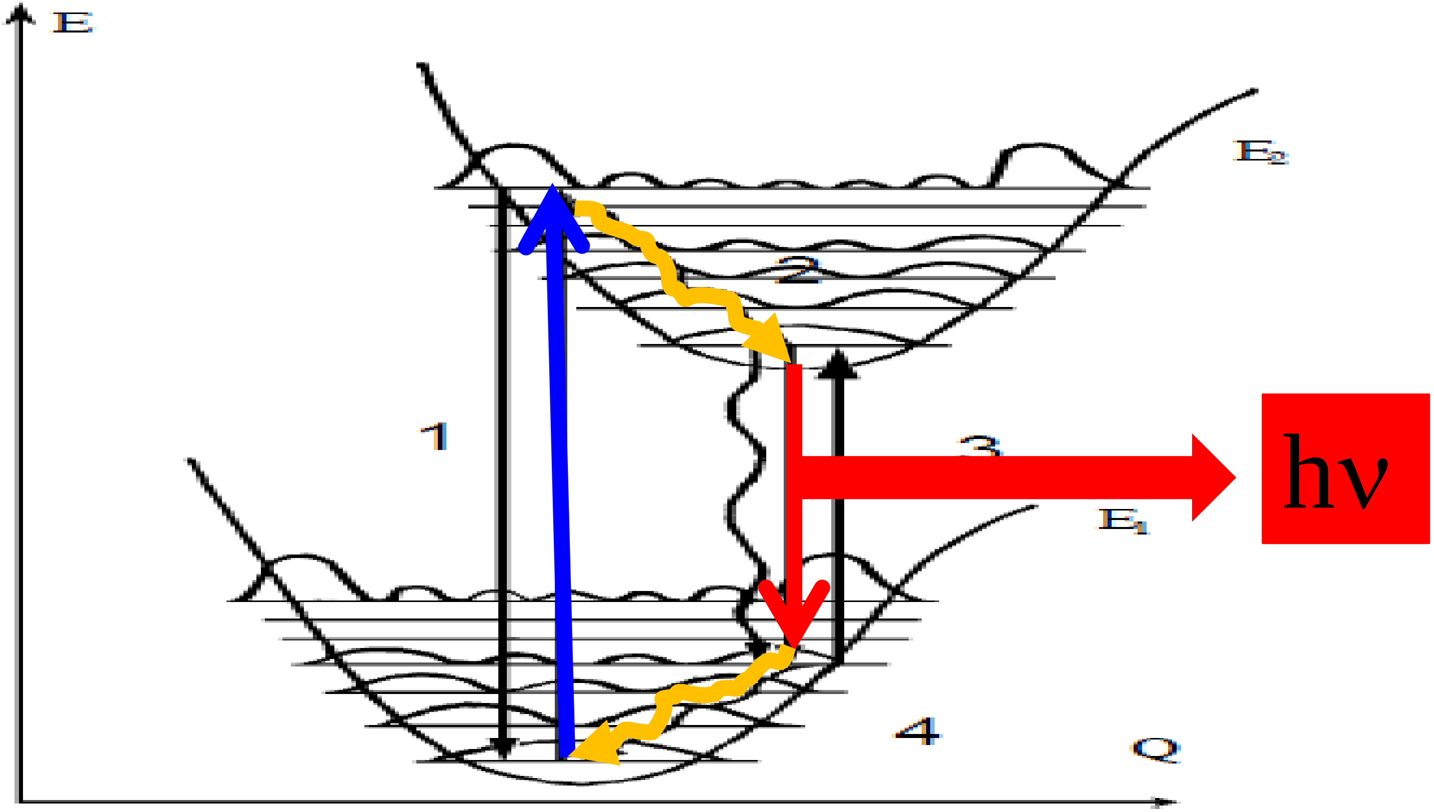
$^2P_{3/2,1/2}$

Electron in a halide box,
Energy $^2S_{1/2} \rightarrow {}^2P_{3/2,1/2} \propto 1/a^2$

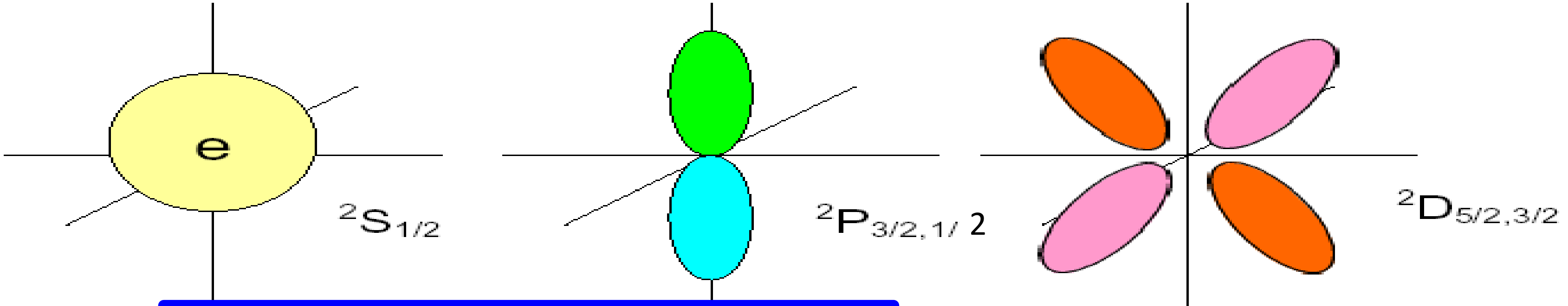
Absorption and Emission Spectra of an F Center in KCl



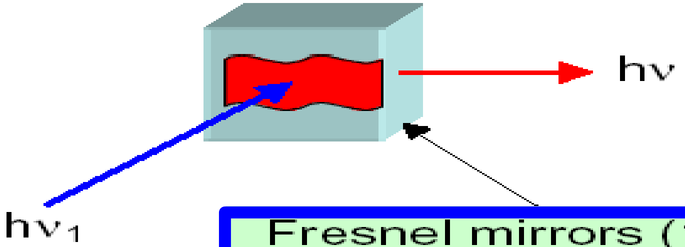
Why the Large Stokes Shift Between Absorption and Emission ?



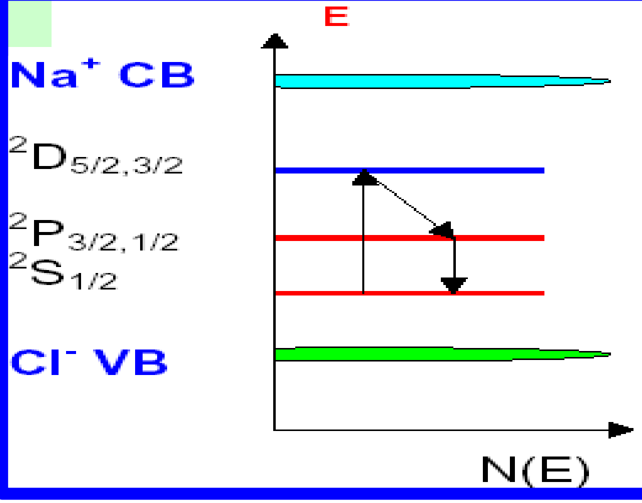
MAKING A F-CENTER LASER FROM A GRAIN OF SALT

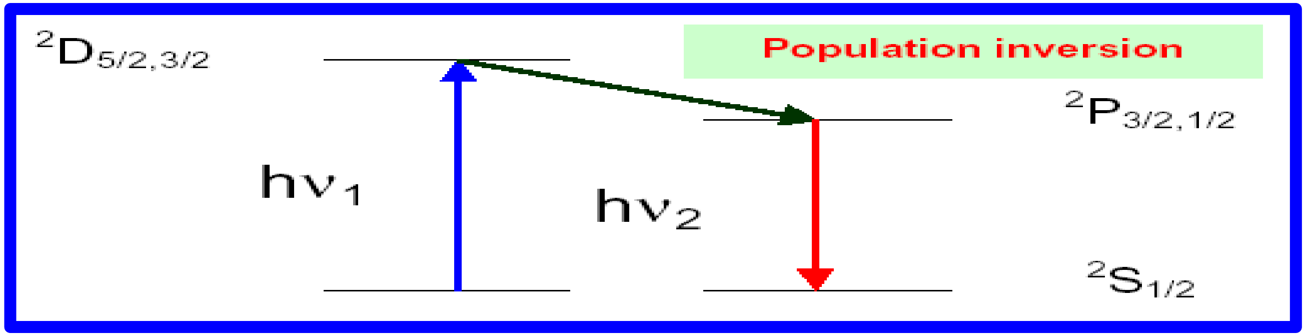


Electron in a halide box,
Energy $^2S_{1/2} \rightarrow {}^2P_{3/2,1/2} \propto 1/a^2$



Fresnel mirrors (100, 99.9% reflecting) on opposite ends of polished crystal





Population inversion