CHEM 548: MATERIALS CHEMISTRY

LECTURE 8: INTRINSIC AND EXTRINSIC POINT DEFECTS

Mon 09/21/2026

Point defects, aliovalent doping, and Kröger–Vink notation

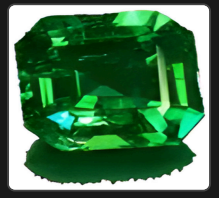
Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry* Ch. 2 §§2.1–2.6; Ch. 3 §3.1

INTRINSIC DEFECTS: LEARNING OBJECTIVES

By the end of this lecture, you should be able to:

Why defects exist	Explain why real crystals always contain defects, even under equilibrium conditions.
The defect types	Identify and describe the major intrinsic point defects: vacancies, interstitials, substitutions (intrinsic site-mixing), Schottky defects, Frenkel defects, and color centers.
Configurational entropy	Understand how configurational entropy drives the presence of defects in crystals.
Defects and properties	Relate defects to important material properties (optical, electronic, mechanical).

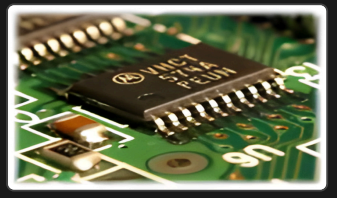
DEFECTS PUT TO WORK



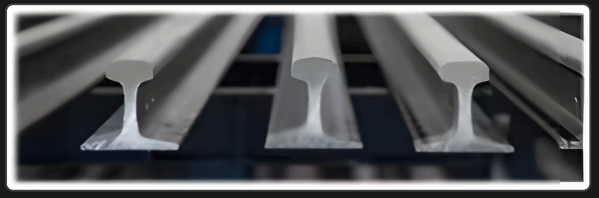
gemstones



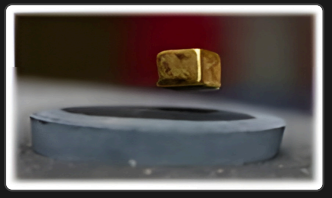
Phosphors



Computer chips

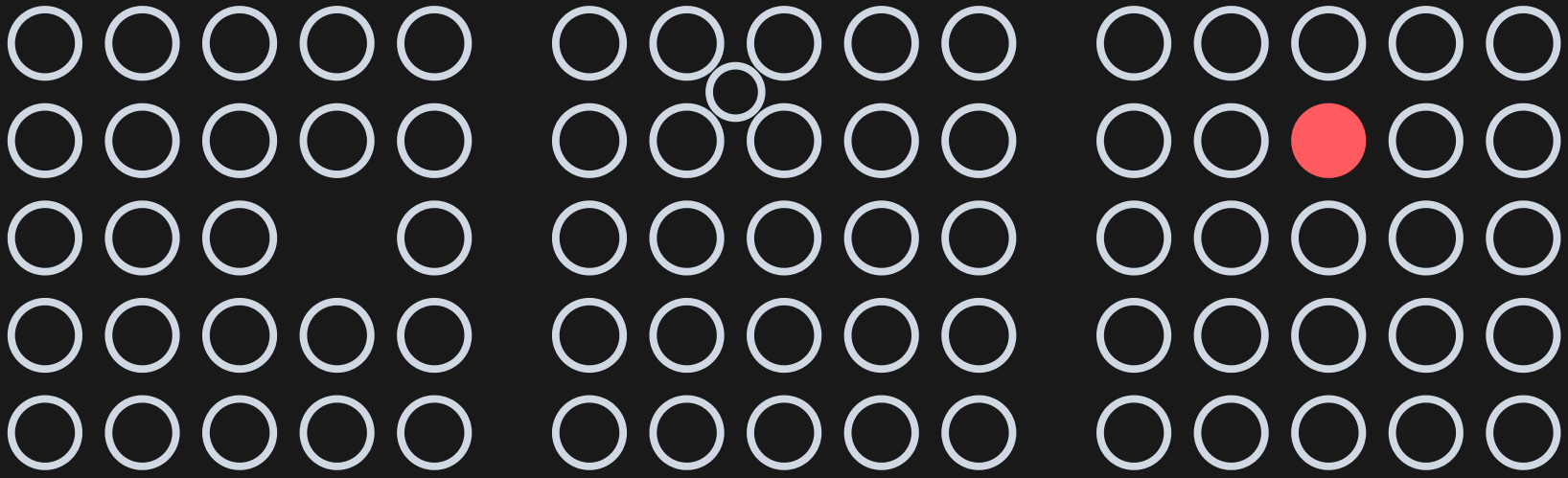


Steel and other alloys



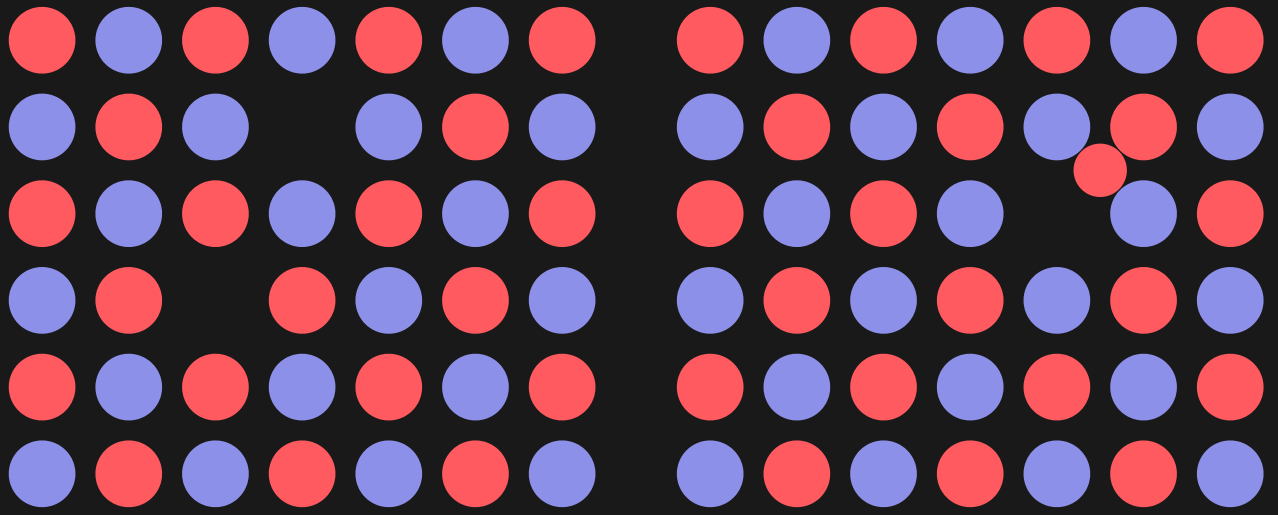
Superconductors

POINT DEFECTS



Per *Solid State Materials Chemistry*, §2.1.

INTRINSIC POINT DEFECTS IN IONIC COMPOUNDS



Schottky Frenkel

Schottky	Cation vacancy + anion vacancy — paired, so the crystal keeps its charge balance
Frenkel	Vacancy + interstitial of the same element — the ion leaves its normal site and occupies an interstitial
Color center	Electron trapped on an anion vacancy

Per *Solid State Materials Chemistry*, §2.2.

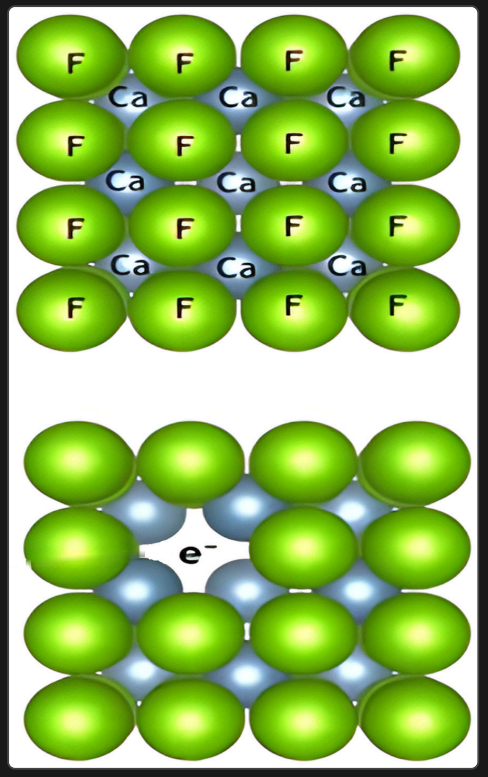
COLOR CENTERS



Fluorite, CaF_2



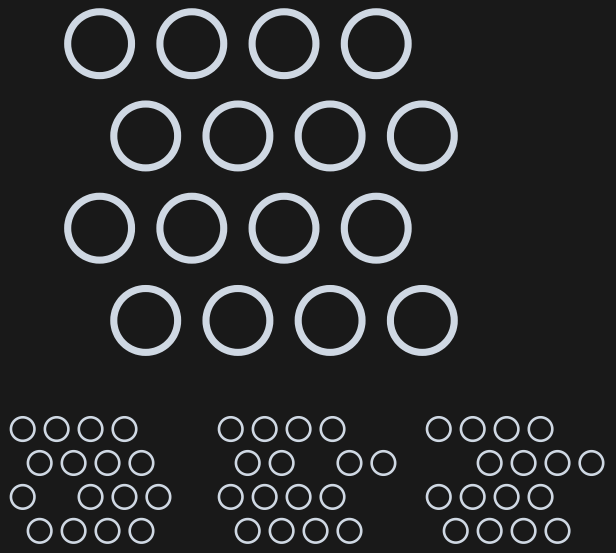
Amethyst, SiO_2



An electron trapped in the anion vacancy, surrounded by Ca^{2+}: the F-center that colors the crystal.

Amethyst is purple quartz colored by Fe^{3+} impurities, not a color-center example. Per *Solid State Materials Chemistry*, §2.2.

THERMODYNAMICS OF DEFECT FORMATION



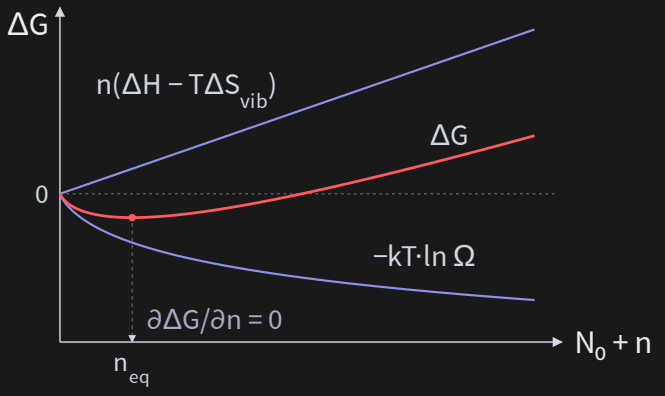
$$\Omega = 1,\ S = \ln \Omega = 0$$

$$\Omega = \frac{(N_0 + n)!}{N_0!\, n!}$$

Defect formation increases the configurational entropy of a crystal

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

$$\Delta G = n(\Delta H - T\Delta S_{vib}) - kT \ln \Omega$$



$$n_{eq} \approx N_0 \exp\left(\frac{\Delta S_{vib}}{k}\right) \exp\left(\frac{-\Delta H}{kT}\right)$$

Per *Solid State Materials Chemistry*, §2.3.

INTRINSIC DEFECTS: SUMMARY

Perfect crystals are an idealization; real crystals always contain defects and surfaces, and the defects are often what makes the material useful.

Defect	What it is
Vacancy	A missing atom.
Interstitial	An extra atom in a normally empty site.
Substitution	An atom on the “wrong” site.
Schottky defect	Paired cation and anion vacancies, so charge stays balanced.
Frenkel defect	An ion displaced from its lattice site into an interstitial site.
Color center	An electron trapped at an anion vacancy, the source of color in many minerals.

Enthalpy cost Making a defect breaks bonds, so it costs enthalpy.

Entropy gain Defects multiply the arrangements open to the crystal, raising the configurational entropy.

The balance $\Delta G = \Delta H - T\Delta S$ sets the equilibrium concentration: defects are always present, and there are more of them at higher T and lower ΔH.

EXTRINSIC DEFECTS: LEARNING OBJECTIVES

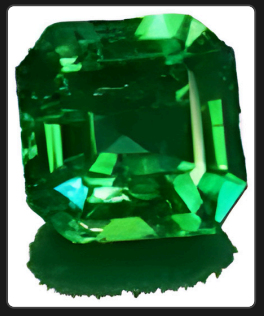
Extrinsic defects	Define and distinguish extrinsic defects from intrinsic defects.
Substitution types	Differentiate isovalent substitution (ruby, emerald, YAG lasers) from aliovalent substitution.
Charge balance	Explain how aliovalent doping stays neutral: excess positive charge → anion interstitials or cation vacancies; a deficit of positive charge → cation interstitials or anion vacancies.
Why doping matters	Describe yttria-stabilized zirconia (an oxide ion conductor), semiconductors (donor/electron versus acceptor/hole doping), and transition metal oxides (variable oxidation states, batteries, superconductivity, magnetoresistance).
Kröger–Vink notation	Interpret it to describe defect types, sites, and charges.

EXTRINSIC DEFECTS (DOPING)

Isovalent	the substituting ion carries the same charge as the ion it replaces, as Cr^{3+} does for Al^{3+} and Nd^{3+} for Y^{3+}
Aliovalent	the substituting ion carries a different charge, so charge neutrality always triggers a compensating change elsewhere in the crystal



Ruby $Al_{2-x}Cr_xO_3$



Emerald $Be_2Al_{2-x}Cr_xSi_6O_{18}$



Nd-YAG laser $Y_{3-x}Nd_xAl_5O_{12}$

Per *Solid State Materials Chemistry*, §2.4.

ALIOVALENT DOPING: HIGHER-CHARGE CATION

A cation of higher charge leaves the crystal with excess positive charge, and if no ion is allowed to change its oxidation state there are two ways to compensate it.

Mechanism	Substitution	Result
Anion interstitials	$\overset{Y^{3+}\text{ for }Ca^{2+}}{CaF_2 \longrightarrow Ca_{1-x}Y_xF_{2+x}}$	$Ca_{1-x}Y_xF_{2+x}$, extra F^- in interstitial sites
Cation vacancies	$\overset{Ca^{2+}\text{ for }Na^{+}}{NaCl \longrightarrow Na_{1-2x}Ca_x\square_xCl}$	$Na_{1-2x}Ca_x\square_xCl$, one Na^+ vacancy per Ca^{2+} added

$\square$ = vacancy

Per *Solid State Materials Chemistry*, §2.4.

ALIOVALENT DOPING: LOWER-CHARGE CATION

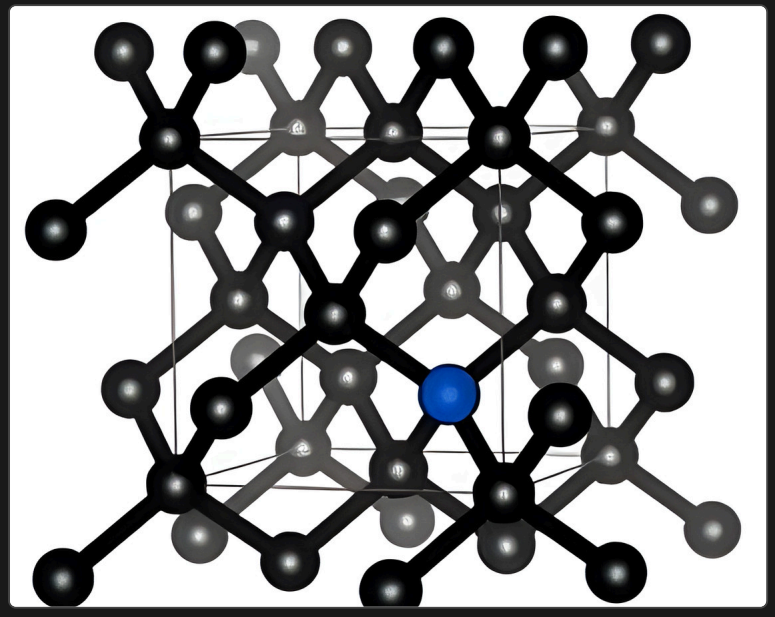
A cation of lower charge leaves the crystal with excess negative charge, and again with every oxidation state fixed there are two ways to compensate it.

Mechanism	Substitution	Result
Cation interstitials	Al^{3+} for Si^{4+} $SiO_2 \longrightarrow Li_xSi_{1-x}Al_xO_2$	$Li_xSi_{1-x}Al_xO_2$, extra Li^+ in interstitial sites
Anion vacancies	Y^{3+} for Zr^{4+} $ZrO_2 \longrightarrow Zr_{1-x}Y_xO_{2-x/2}\square_{x/2}$	$Zr_{1-x}Y_xO_{2-x/2}\square_{x/2}$, one O^{2-} vacancy per two Y^{3+}

□ = vacancy

Per *Solid State Materials Chemistry*, §2.4.

ALIOVALENT SEMICONDUCTOR DOPING



Donor (electron) doping	the substituting atom has more valence electrons than the host, as P does for Si; equivalent to reducing the lattice
Acceptor (hole) doping	the substituting atom has fewer valence electrons than the host, as B does for Si; equivalent to oxidizing the lattice

Per *Solid State Materials Chemistry*, §2.4.

CONTROLLING OXIDATION STATE: OXIDATION

Compounds of the transition metals are very sensitive to the oxidation state of the cation, so doping that raises it is a way of controlling the properties.

Mechanism	Substitution	Oxidation state
Cation vacancies	$\xrightarrow{\text{remove } Li^{+}}$ $LiCoO_2 \longrightarrow Li_{1-x}CoO_2$	$Co^{+3} \rightarrow Co^{+(3+x)}$
Anion interstitials	$\xrightarrow{\text{add } O^{2-}}$ $La_2CuO_4 \longrightarrow La_2CuO_{4+x}$	$Cu^{+2} \rightarrow Cu^{+(2+2x)}$
Aliovalent doping with a lower-valent cation	$\xrightarrow{Sr^{2+} \text{ for } La^{3+}}$ $La_2CuO_4 \longrightarrow La_{2-x}Sr_xCuO_4$	$Cu^{+2} \rightarrow Cu^{+(2+x)}$

Per *Solid State Materials Chemistry*, §2.4.

CONTROLLING OXIDATION STATE: REDUCTION

Compounds of the transition metals are very sensitive to the oxidation state of the cation, so doping that lowers it is a way of controlling the properties.

Mechanism	Substitution	Oxidation state
Cation interstitials	insert Li^+: $TiS_2 \longrightarrow Li_xTiS_2$	$Ti^{+4} \rightarrow Ti^{+(4-x)}$
Anion vacancies	remove O^{2-}: $WO_3 \longrightarrow WO_{3-x}$	$W^{+6} \rightarrow W^{+(6-2x)}$
Aliovalent doping with a higher-valent cation	La^{3+} for Ca^{2+}: $CaMnO_3 \longrightarrow Ca_{1-x}La_xMnO_3$	$Mn^{+4} \rightarrow Mn^{+(4-x)}$

Per *Solid State Materials Chemistry*, §2.4.

KRÖGER–VINK NOTATION

One symbol names an extrinsic defect in three parts: what the defect is, where it sits, and the charge it carries relative to the host site.



•	charge +1	′	charge −1
••	charge +2	″	charge −2
•••	charge +3	‴	charge −3
×	charge 0		

Per *Solid State Materials Chemistry*, §2.6.

KRÖGER–VINK EXAMPLES: OXIDATION

Mechanism	Reaction	Kröger–Vink symbol
Cation vacancies	Remove Li^+: $LiCoO_2 \longrightarrow Li_{1-x}CoO_2$	v'_{Li}
Anion interstitials	Add O^{2-}: $La_2CuO_4 \longrightarrow La_2CuO_{4+x}$	O''_i
Aliovalent doping with a lower-valent cation	Sub. Sr^{2+} for La^{3+}: $La_2CuO_4 \longrightarrow La_{2-x}Sr_xCuO_4$	Sr'_{La}

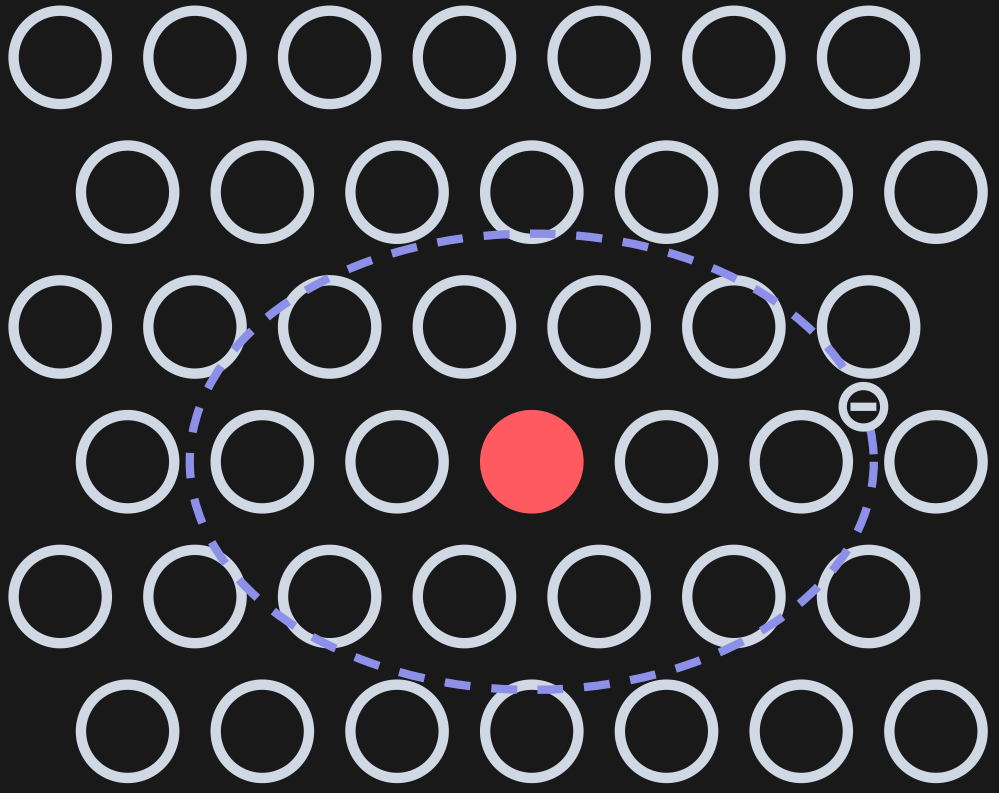
Per *Solid State Materials Chemistry*, §2.6.

KRÖGER–VINK EXAMPLES: REDUCTION

Mechanism	Reaction	Kröger–Vink symbol
Cation interstitials	Insert Li^+: $TiS_2 \longrightarrow Li_xTiS_2$	$Li_i^{\bullet}$
Anion vacancies	Remove O^{2-}: $WO_3 \longrightarrow WO_{3-x}$	$v_O^{\bullet\bullet}$
Aliovalent doping with a higher-valent cation	Sub. La^{3+} for Ca^{2+}: $CaMnO_3 \longrightarrow Ca_{1-x}La_xMnO_3$	$La_{Ca}^{\bullet}$

Per *Solid State Materials Chemistry*, §2.6.

DONOR DOPING IN SILICON



- P core: one extra proton, +1 relative to Si
- P's extra electron on the dashed orbit, −1
- host lattice atom (Si)

- Relative to Si, P brings one extra proton (+1) and one extra electron (−1)
- Bound, low T: electron in a hydrogen-like orbit, whole center neutral. The +1 and −1 cancel: $\mathrm{P}_{\mathrm{Si}}^{\times}$, where × means zero effective charge
- Ionized: electron free, nothing cancels the extra proton, so the site is +1: $\mathrm{P}_{\mathrm{Si}}^{\bullet}$, plus the free electron e'
- $\mathrm{P}_{\mathrm{Si}}^{\times} \rightarrow \mathrm{P}_{\mathrm{Si}}^{\bullet} + e'$: charge balances, about 45 meV in Si

Per *Solid State Materials Chemistry*, §3.1.

EXTRINSIC DEFECTS: SUMMARY

Extrinsic defects arise from putting foreign atoms into a lattice, and whatever charge they carry, the crystal has to compensate.

Substitution	Compensation	Key examples
Isovalent	None needed: no net charge imbalance.	Ruby and emerald coloration, YAG lasers.
Aliovalent, compensated by defects	Interstitials or vacancies on the sublattice that restores neutrality.	Y-stabilized ZrO_2 for oxygen conduction, semiconductor doping (n-type, p-type).
Aliovalent, compensated by redox	A transition metal changes oxidation state instead.	Battery cathodes ($LiCoO_2$), superconductors (La_2CuO_4), bronzes (WO_{3-x}), colossal magnetoresistance oxides.

Kröger–Vink notation A systematic language for defect chemistry: the defect species, the site it sits on, and its effective charge.

PRACTICE QUESTIONS

Work the Lecture 8 practice questions before the next class. They cover equilibrium vacancy concentrations in metals, Schottky defect counts in ionic solids, oxidation states in mixed-valent oxides, and Kröger–Vink notation for point defects.

Open the Lecture 8 practice questions

Every question carries a worked explanation, so you can check your reasoning as you go.