

Non-stoichiometric compounds

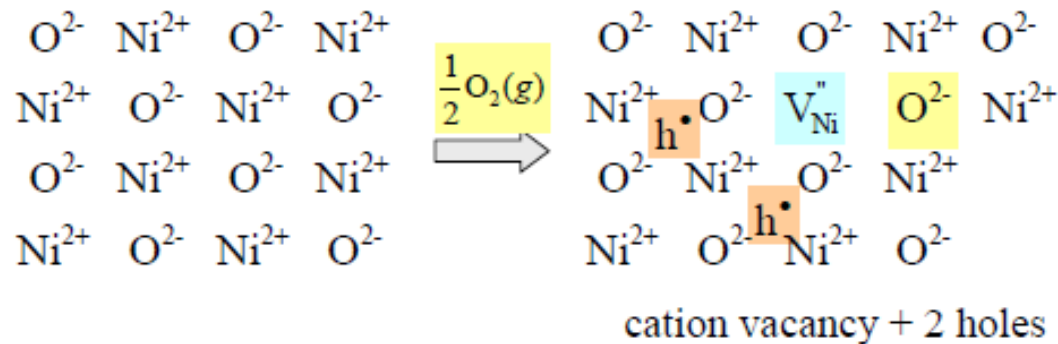
Non-stoichiometry

While some of the compounds become unstable at small deviations from stoichiometric composition (e.g. NaCl), other compounds can exhibit large deviations from stoichiometric composition or even be unstable at the stoichiometric composition (e.g. FeO - wüstite phase).



For a transfer of oxygen to a metal oxide MO: $\frac{1}{2}O_2(g) \leftrightarrow O_O^x + V_M$ (transfer of neutral O)

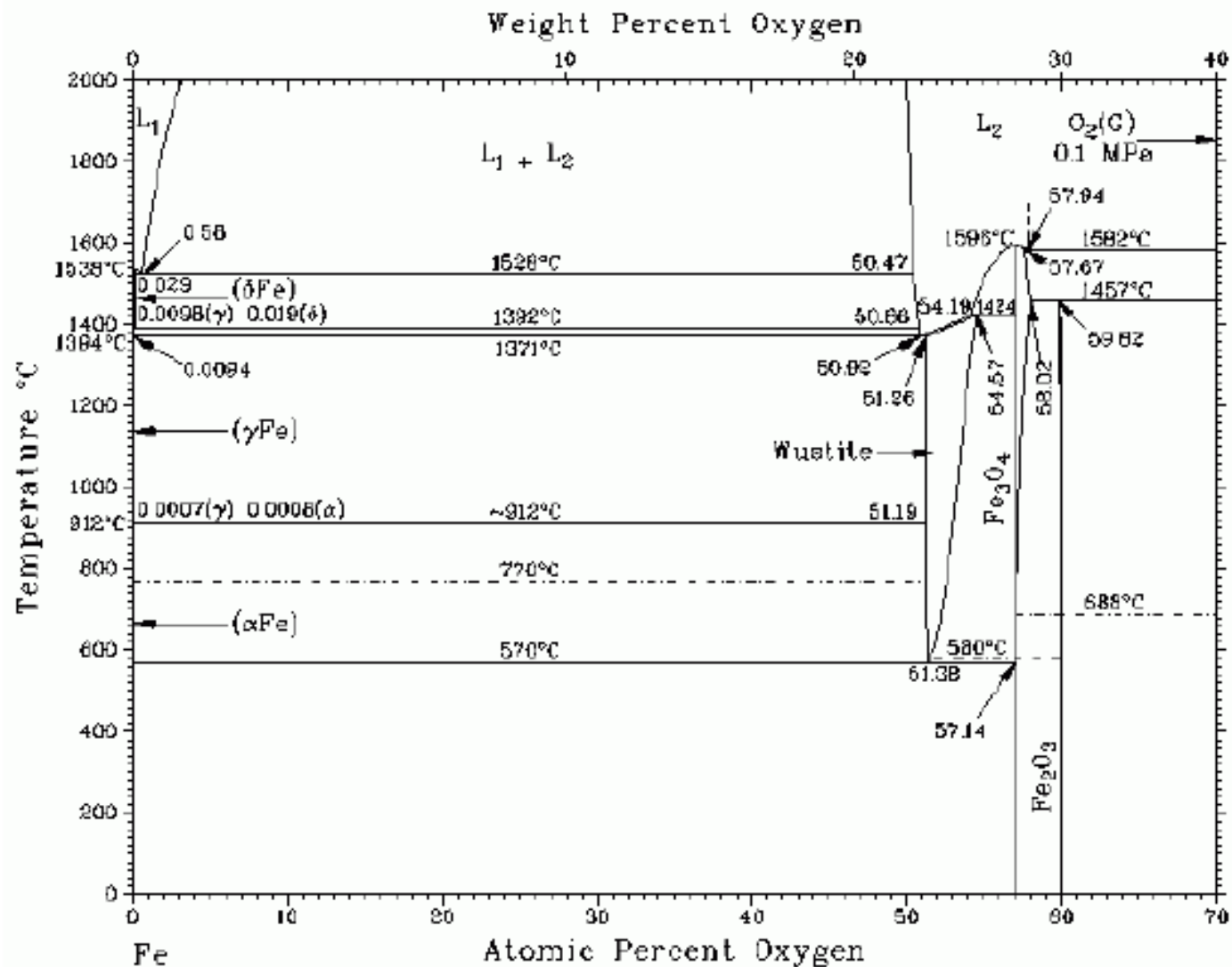
But if the crystal is ionic, O will accept 2 e- that should come from metal that is already ionized, e.g., for NiO: $\frac{1}{2}O_2(g) \leftrightarrow O_O^x + 2h^\bullet + V_{Ni}''$



Ni^{2+} can then transform into Ni^{3+} (2 Ni ions have to be transformed for each vacancy) (equivalent to solution of Ni_2O_3 in NiO)

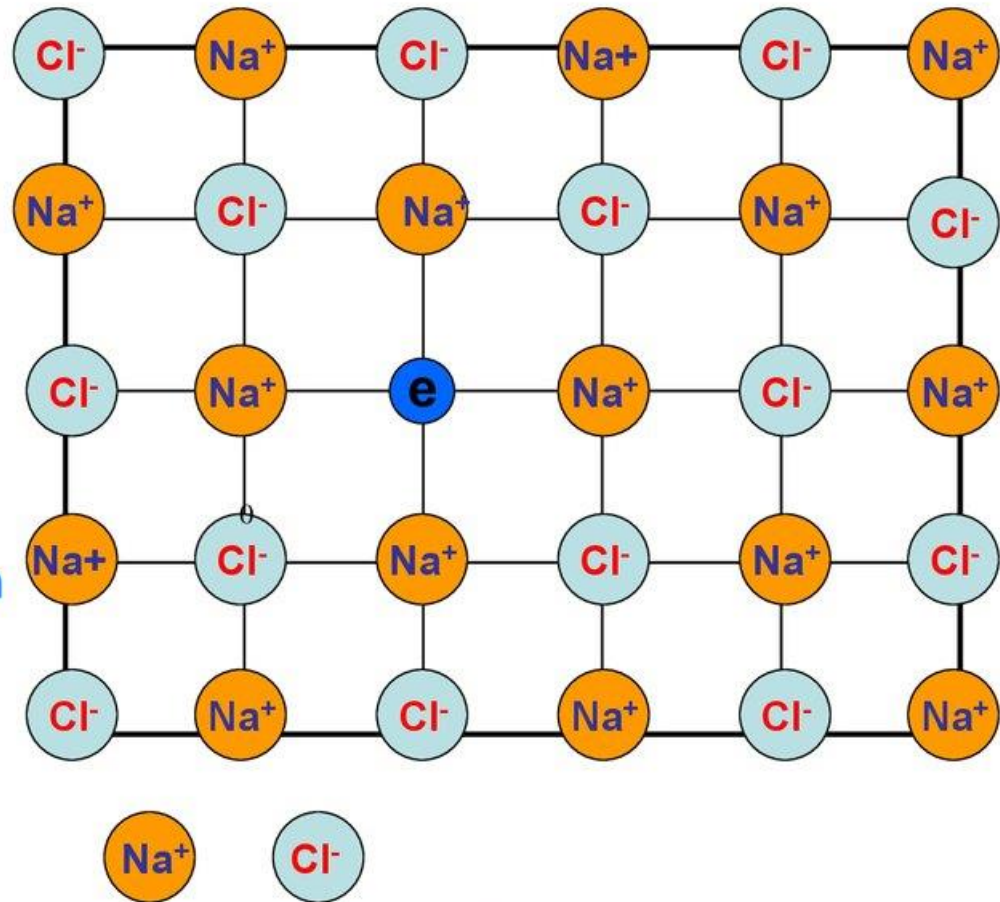
This scenario works for transition metals (e.g., Fe, Ti, Cu, Ni), where the ionization energy is low, but not for metals with high ionization energy (e.g. Na or K)

Non-stoichiometry



Color centres F-centres

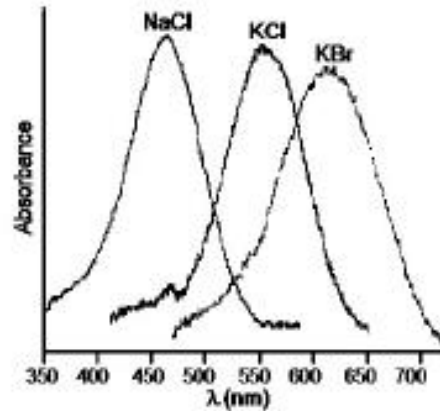
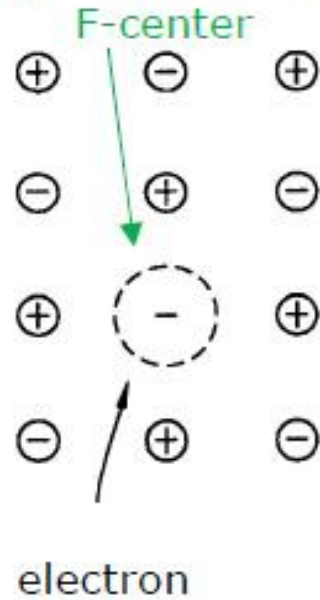
- NaCl exposed to Na vapor.
- Absorbed Na ionized.
- Electron diffuses into crystal and occupies an anionic vacancy.
- Equal number of Cl⁻ move outwards to the surface.
- Classical example of particle in a box.



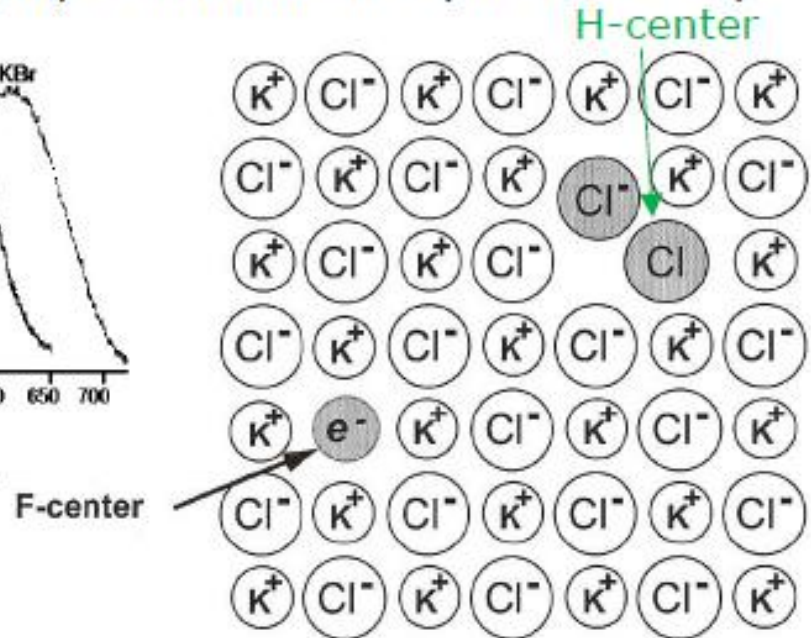
Nonstoichiometric
greenish yellow

Color Centers

Crystals of alkali halides become brightly colored when exposed to X-rays.



A color center is known as a Farbenzentrum (**F-center**).



Electron Spin Resonance (ESR) spectroscopy confirms the presence of unpaired electrons trapped at vacant lattice (anion site).



A **H-center** may also be formed by heating NaCl in Cl_2 gas, with the Cl_2^- ion occupying an anion site.