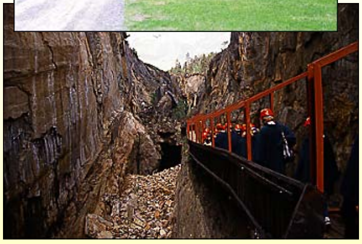
Color in materials

Pigments



Black body radiation
Incandescence

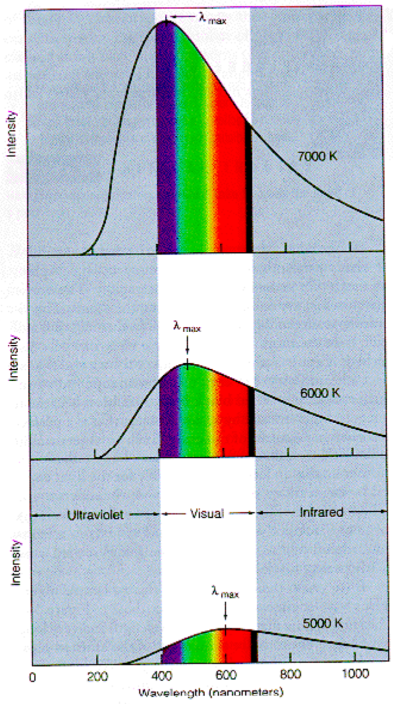
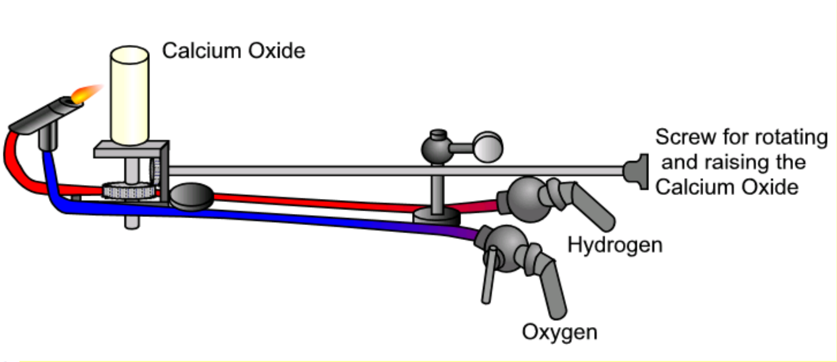
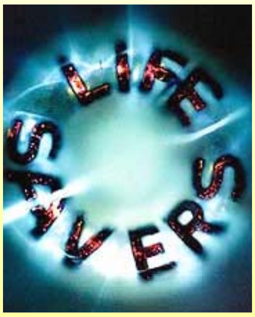


FIGURE 6-6
Black body radiation from three objects of slightly different temperature demonstrates how a hotter object (top) emits more total energy than a cooler object (bottom). Also, the hotter body emits more short-wavelength radiation and thus looks blue, while the cooler object emits more long-wavelength radiation and thus looks redder. Note that the wavelength of maximum intensity, λ_{max}, shifts to longer wavelengths as temperature falls.

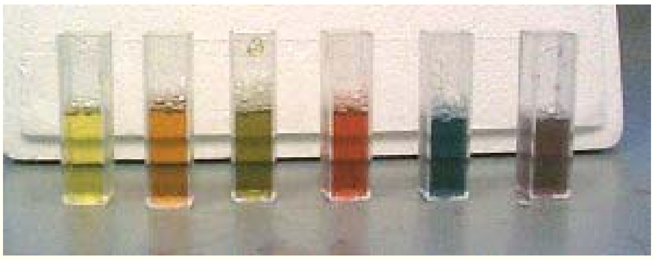


Luminescence

Triboluminescence

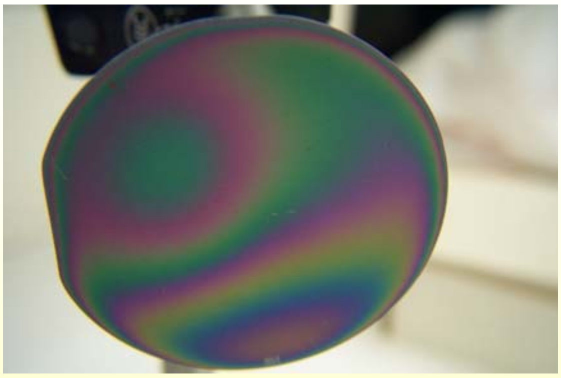


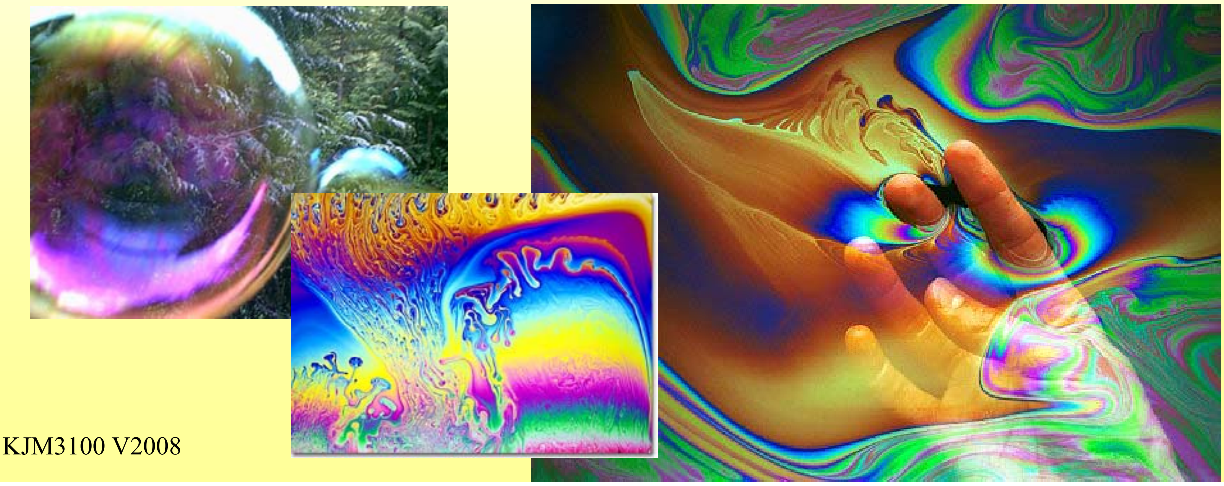
The colour of silver nanoparticles depends on the shape of the particles.



A collaborative group of DuPont-led scientists have discovered an innovative way to advance electronics applications through the use of DNA that sorts carbon nanotubes. (Pictured) Unsorted nanotubes in solution appear in black (far left). Conducting nanotubes are pinkish in color, semiconducting ones greenish.

Interference colours

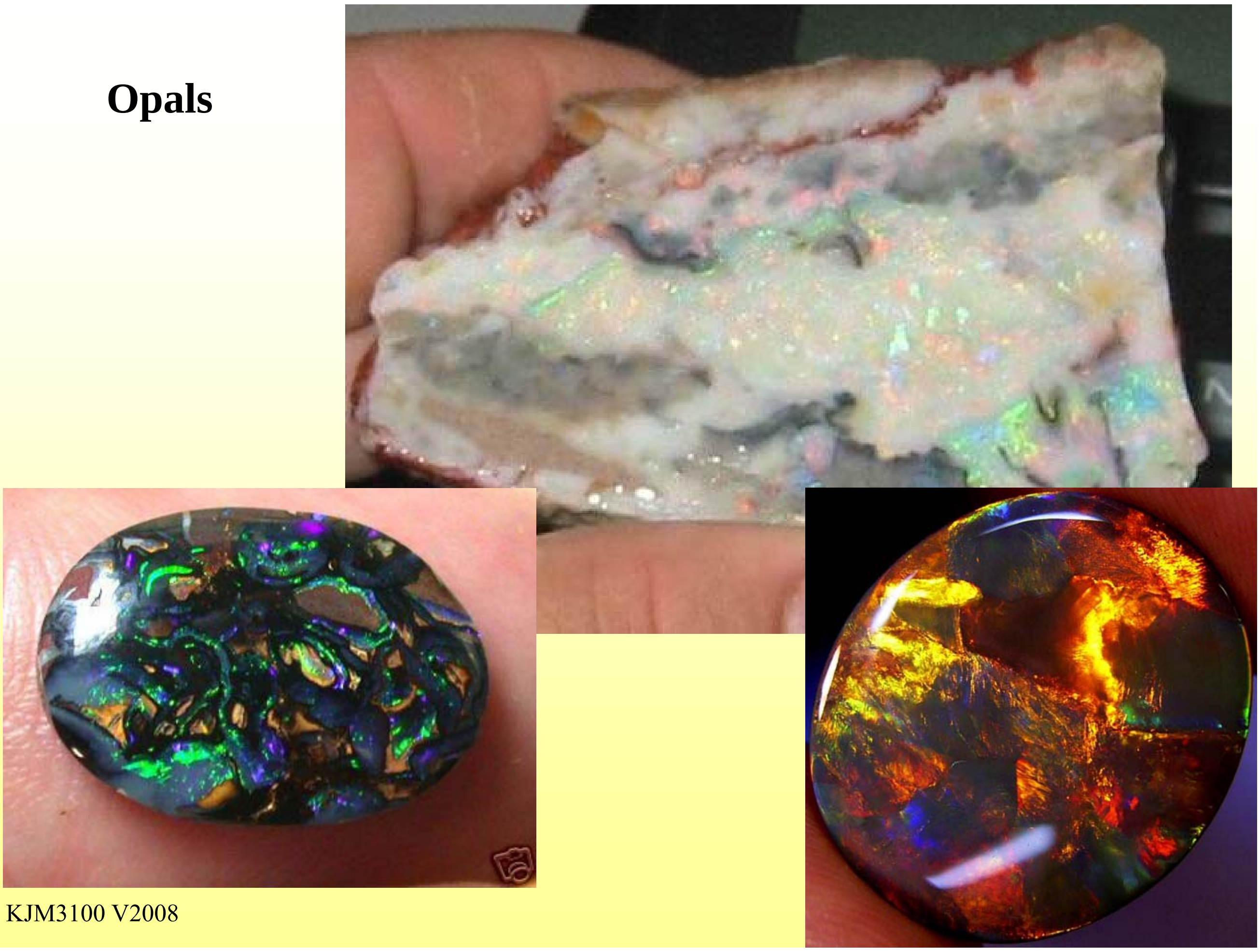


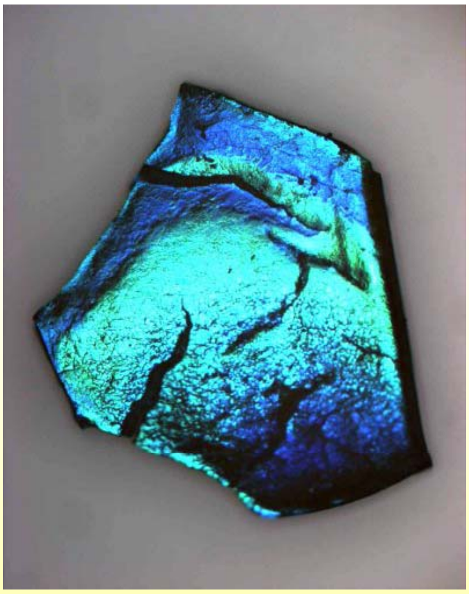


Liquid crystals

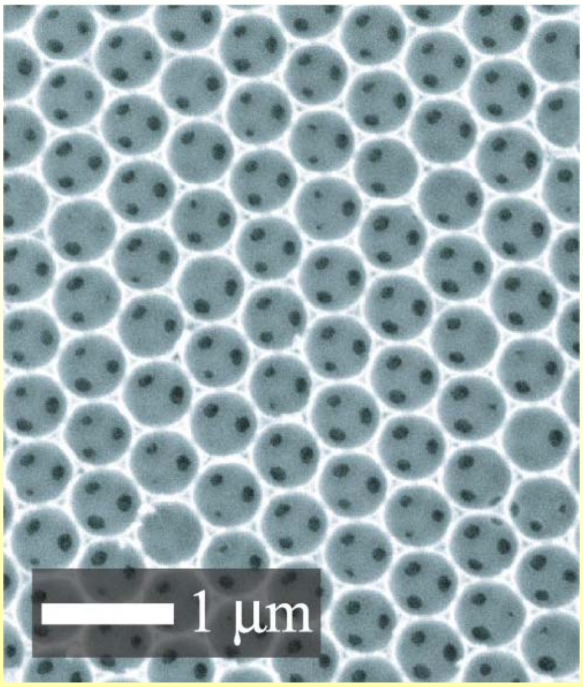
Mood jewelry

Opals





A photograph of a photonic crystal that is about 2 millimeters across. The blue iridescence is caused by light reflections off the ordered stack of air spheres. (Credit: COPS)



An SEM image of the inverse opal structure. The crystal consists of an ordered array of voids in a solid material. (Credit: COPS)

Butterfly wings

Monarch Butterfly
Wing Scale

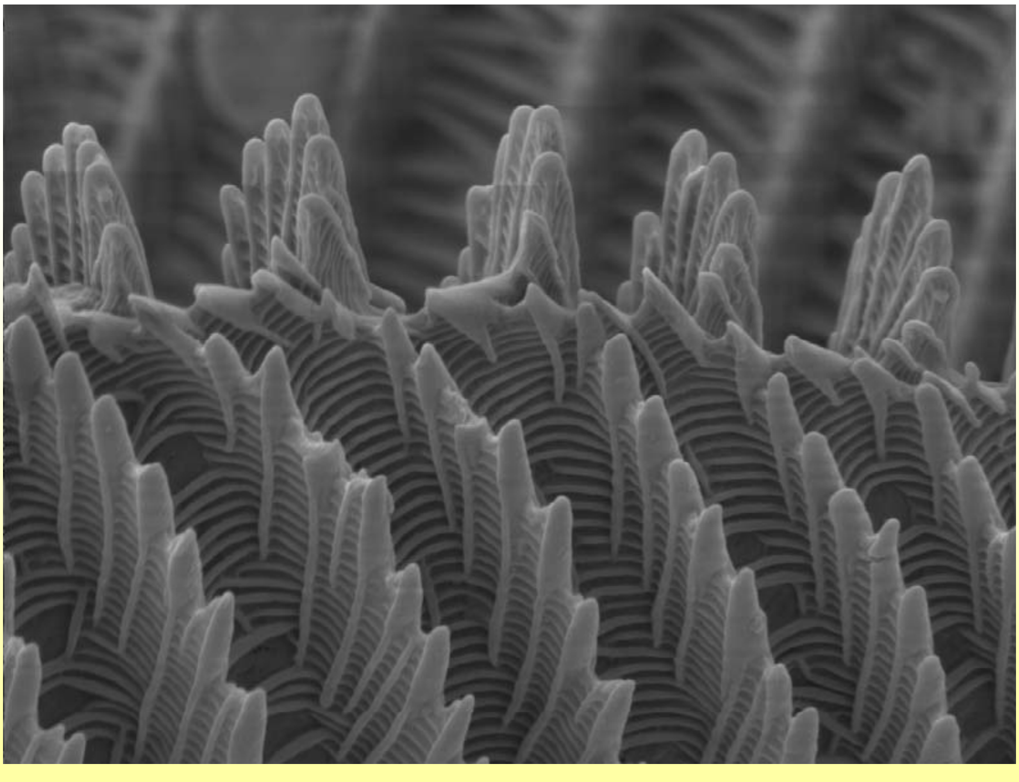
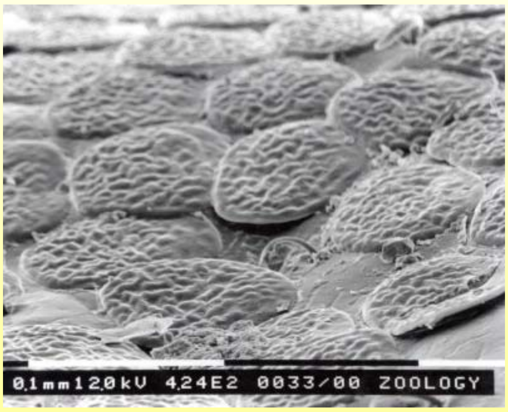
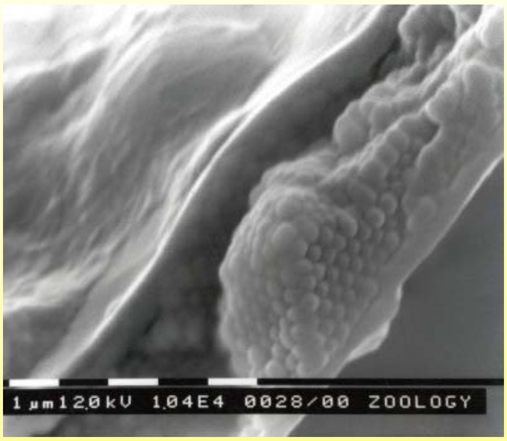


Image showing the architecture of the tip of a single scale from the wing of a male Monarch butterfly. Taken as an ultra high definition scan using the ESEM in HiVac mode. Original magnification about 30,000x. The vertical ridges are 1 to 2 micrometers apart.

Beetle perfects artificial opal growth

An anterior view of the weevil Pachyrhynchus argus, a small beetle found in forests in north-eastern Australia. Its body appears a metallic green colour from all angles thanks to a photonic crystal structure that resembles opal. (Credit: Andrew Parker)





The vivid colour comes courtesy of thin, flat scales which occur in patches over the beetle's body. The scales consist of an outer shell and an inner structure that contains layers of 250 nm diameter transparent spheres.

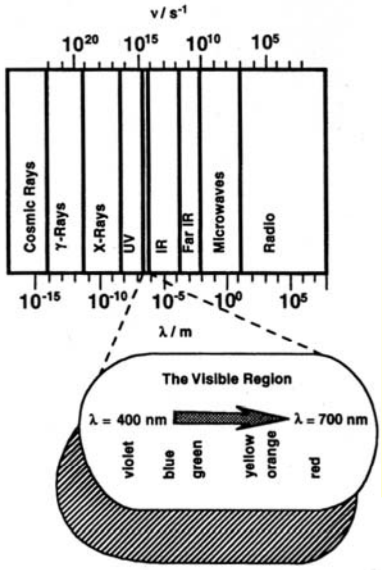
Kurt Nassua, in his book *The Physics and Chemistry of Color*, identifies 15 different causes of color.

1. **Incandescence**
2. **Gas Excitations**
3. **Color from Vibrations and Rotations**
4. **Transition Metals in a Ligand Field**
5. **Organic Molecules**
6. **Charge Transfer**
7. **Metals**
8. **Semiconductors**
9. **Doped Semi-conductors**
10. **Color Centers**
11. **Dispersive Refraction**
12. **Polarization**
13. **Scattering**
14. **Interference**
15. **Diffraction**

Table 1. **Twelve types of color in minerals**

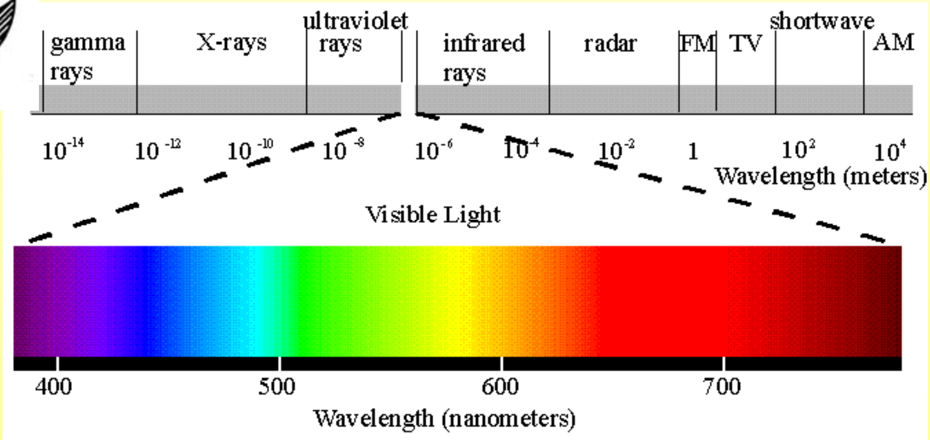
Color Cause	Typical minerals	Formalism
Transition metal compounds	Almandite, malachite, turquoise	Crystal field theory
Transition metal impurities	Citrine, emerald, ruby	Crystal field theory
Color centers	Amethyst, fluorite, smoky quartz	Crystal field theory
Charge transfer	Blue sapphire, crocoite, lazurite	Molecular orbital theory
Organic materials	Amber, coral, graphite	Molecular orbital theory
Conductors	Copper, iron, silver	Band theory
Semiconductors	Galena, proustite, pyrite, sulfur	Band theory
Doped semiconductors	Blue diamond, yellow diamond	Band theory
Dispersion	"Fire" in faceted gems	Physical optics
Scattering	Moonstone, "stars", "eyes"	Physical optics
Interference	Iridescent chalcopyrite	Physical optics
Diffraction	Opal	Physical optics

Electromagnetic spectrum



Conversions:
wavelength (nm) = 1239.9/energy (eV)
(energy (eV) = 1239.9/wavelength (nm))

wavelength (cm^{-1}) = 10^7/wavelength (nm)



Energy in electronic energy levels, vibrational and rotational energy levels.
500 nm = 20000 cm^{-1}
Energy transitions involving valence electrons may be in the visible spectrum
Energy transitions involving closed shell electrons are in the UV/X-ray region

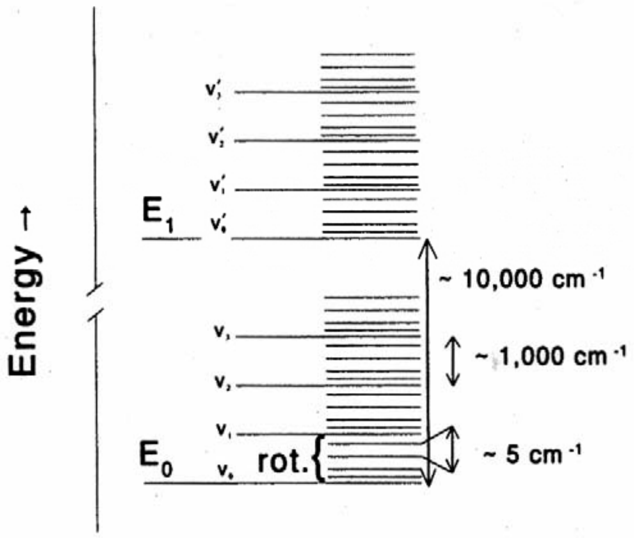
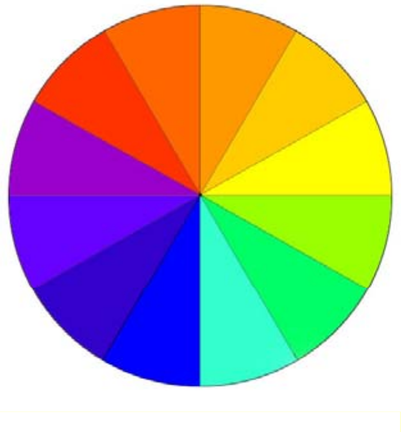
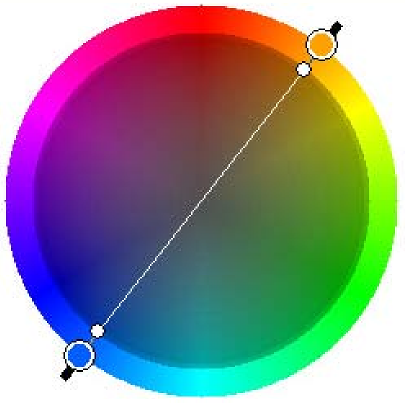
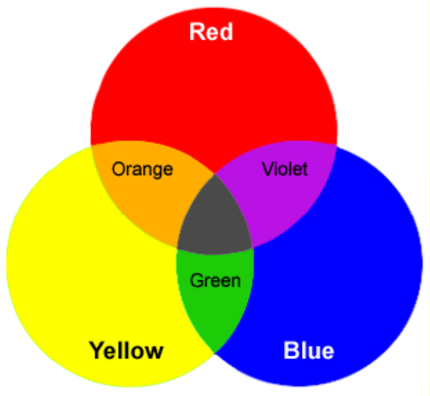


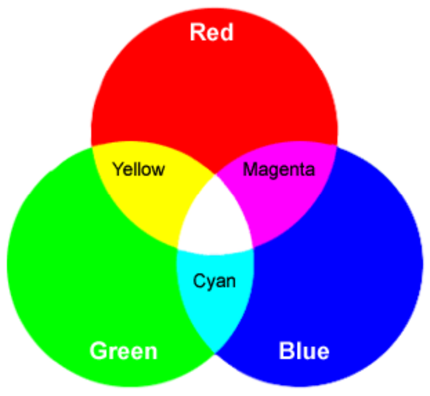
Figure 2.2. Schematic representations of the relative spacings of electronic energy levels (marked E_0 and E_1), vibrational energy levels (marked v_0, v_1, . . . and v_0', v_1', . . .) and rotational energy levels (marked rot.). The approximate energies are given in units of cm^{-1}, called **wavenumbers**, and abbreviated $\bar{\nu}$, where $\bar{\nu} = 1/\lambda$. 1 cm^{-1} = 1.97 × 10^{-5} eV = 3.15 × 10^{-24} J.

Colour wheel



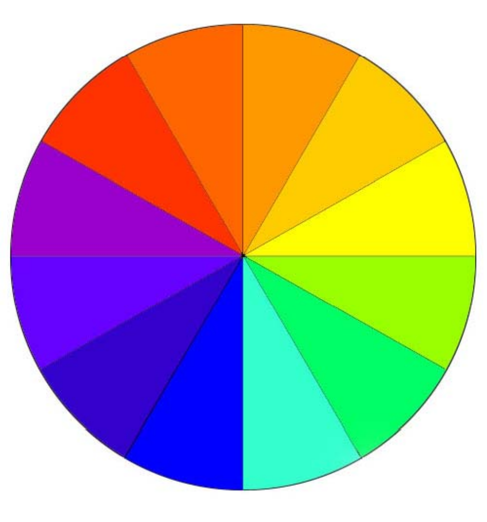






Transmission/reflection

The absorbed and transmitted colours are complementary



Electronic transitions in atoms

Na: $1s^2 2s^2 2p^6 3s^1$

Wavelengths of emitted light: 589.1 and 589.6 nm (yellow)
Neon light, lasers (e.g. Ar-laser)

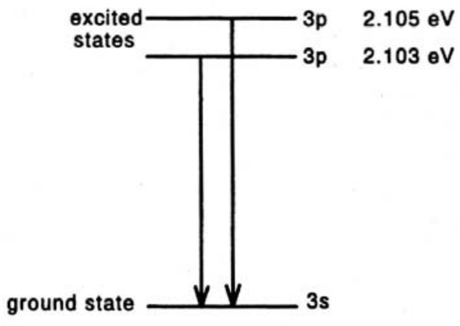


Figure 2.5. The electronic energy levels of Na. Excitation is caused by heat and emission of yellow light results.

Nordlys, Aurora borealis

Emission spectra

In general emission spectra of gases are more narrow than for solids. Due to low density (fewer collisions) in gases.

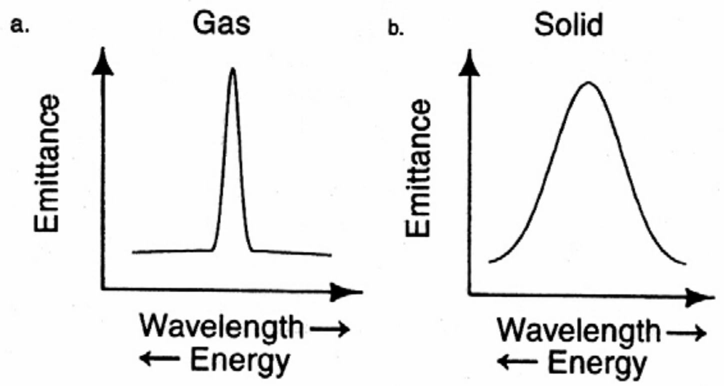


Figure 2.6. Schematic emissions from (a) a gas and (b) a solid.

Black-body radiation
Incandescence

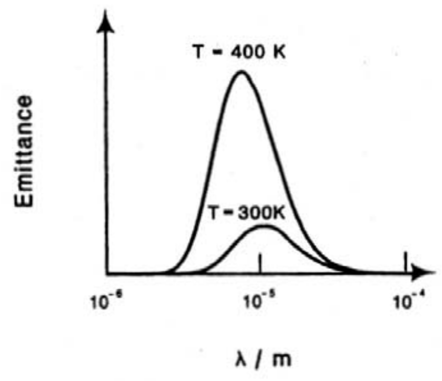


Figure 2.7. Typical ideal black-body radiation spectra at two temperatures. Note the increase in the emitted radiation (curve area) and the shift in the peak to lower wavelength (higher energy) when the temperature is increased.

Ideally does not reflect or transmit light
Independent on material.
Frequency (and intensity) increase with increasing temperature

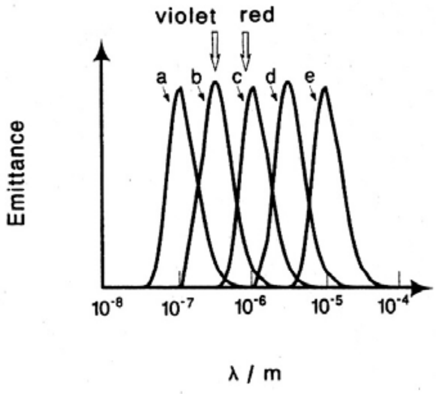


Figure 2.8. Black-body radiation as a function of temperature, highlighting how the color changes as the temperature changes. The corresponding temperatures of the black bodies are a, $T = 30{,}000$ K; b, $T = 10{,}000$ K; c, $T = 3000$ K; d, $T = 1000$ K; e, $T = 300$ K. To have all the peaks of the same area, they have been scaled as follows: a, ×1; b, ×270; c, $\times 10^5$; d, $\times 2.7 \times 10^7$; e, $\times 10^{10}$. Note the shift in the peak to longer wavelength (lower energy) and the smaller peak area with lower temperature.

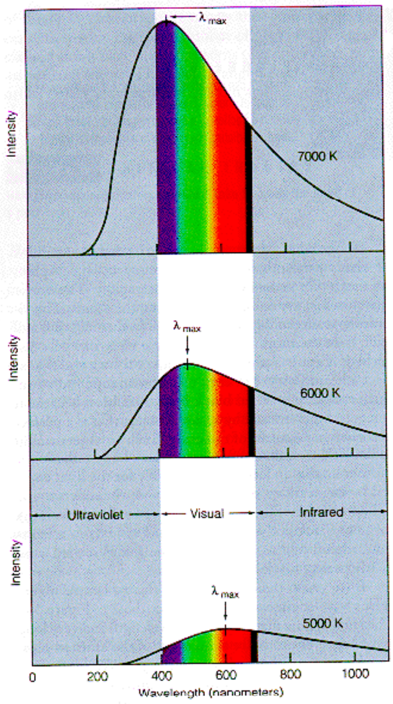
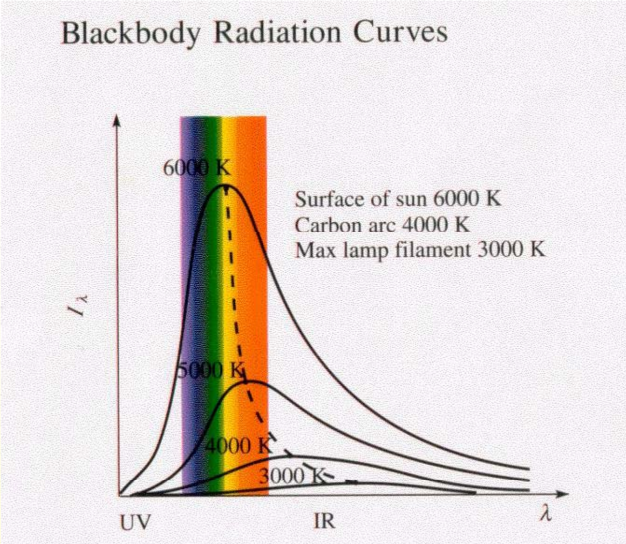


FIGURE 6-6
Black body radiation from three objects of slightly different temperature demonstrates how a hotter object (top) emits more total energy than a cooler object (bottom). Also, the hotter body emits more short-wavelength radiation and thus looks blue, while the cooler object emits more long-wavelength radiation and thus looks redder. Note that the wavelength of maximum intensity, λ_{max}, shifts to longer wavelengths as temperature falls.



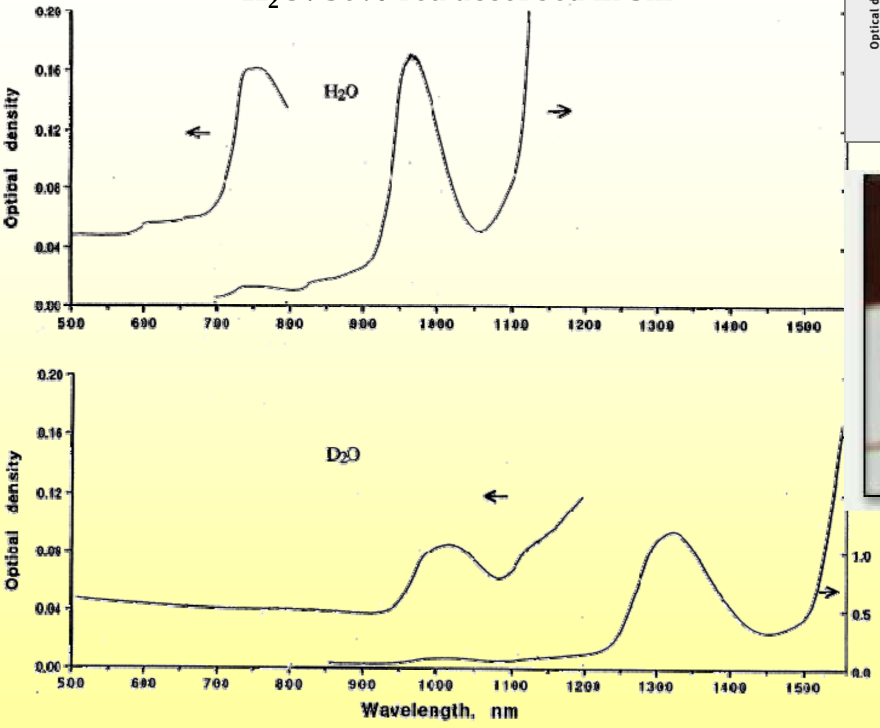
T, K	oC	Subjective color
750	480	faint red glow
850	580	dark red
1000	730	bright red, slightly orange
1200	930	bright orange
1400	1100	pale yellowish orange
1600	1300	yellowish white
>1700	>1400	white (yellowish if seen from a distance)

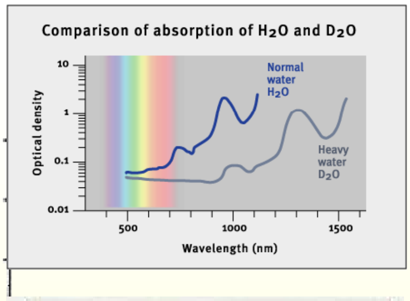
The perceived color of heated solid bodies

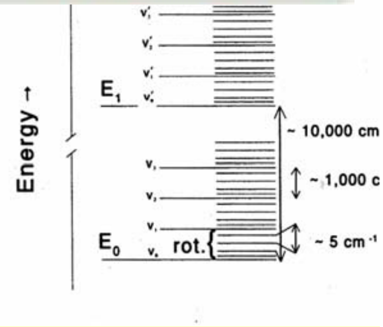
Why does a candle give more light than a hydrogen/oxygen flame?

Vibrational transitions.

H_2O: 56% red absorbed in 3m




Comparison of absorption of H_2O and D_2O

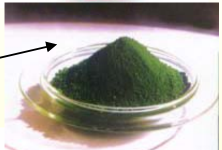


Crystal field colours

Ruby (red)

Al_2O_3 (corundum) w. ca. 1w%Cr^{3+}
Strong crystal field

Cr_2O_3: Green



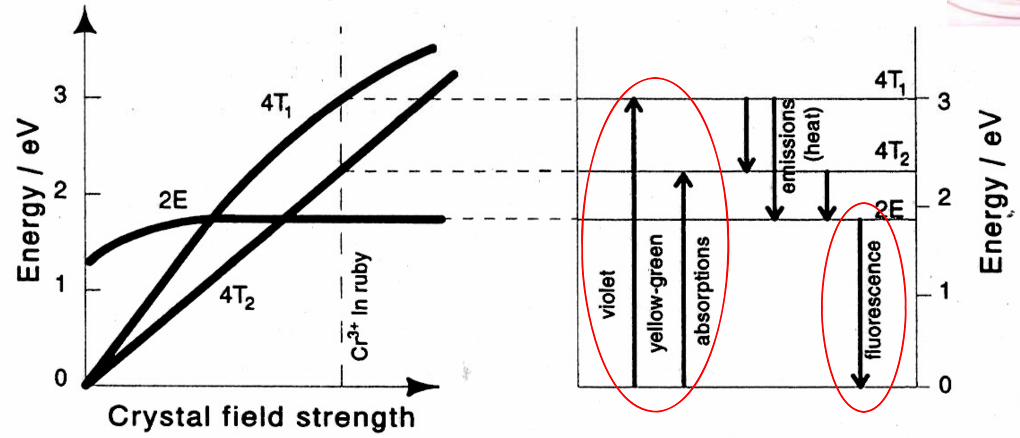
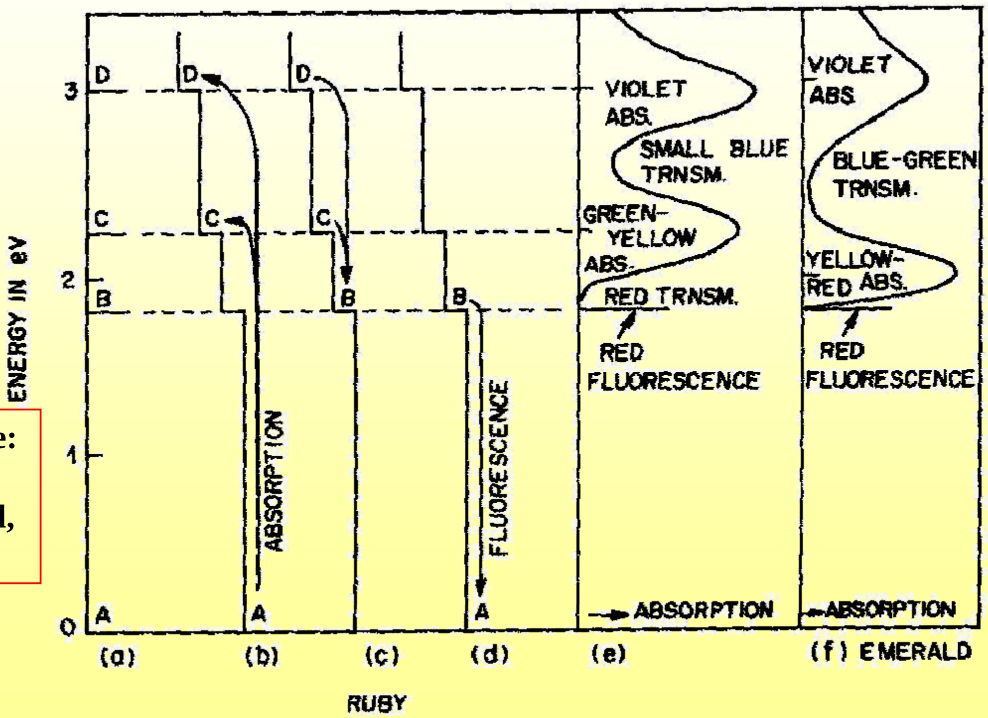


Figure 2.9. The effect of crystal field strength on the splitting of the energy levels of Cr^{3+} ions in a lattice. Styled after K. Nassau (1980), *Scientific American,* October 1980, 134.

Emerald; green variant of beryl, Also caused by Cr^{3+}

Beryl: $Be_3Al_2Si_6O_{18}$



Alexandrite: Cr^{3+} in chrysoberyl, $BeAl_2O_4$

Aquamarin: Fe^{3+} in beryl

Citrine: Fe^{3+} in SiO_2

Beryl:
$Be_3Al_2Si_6O_{18}$
Colourless

Jadeite: Fe^{3+} in $NaAl(SiO_3)_2$

Crystal field, pure composition

Azurite, $Cu_3(CO_3)_2(OH)_2$

Garnet, e.g. $Fe_3Al_2(SiO_4)_2$

Malachite, $Cu_2CO_3(OH)_2$

Rhodochrosite, $Mn(CO_3)$

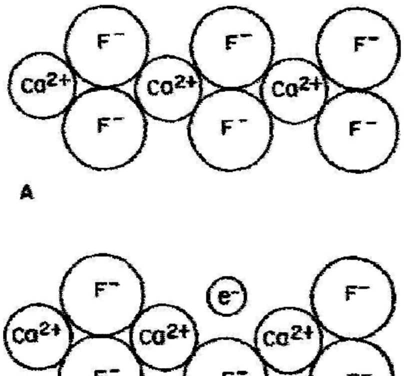
Colour centres (F-centres)

The unpaired electron which produces color by light absorption into excited states does not have to be located on a transition element ion; under certain circumstances it can be located on a nontransition-element impurity ion or on a crystal defect such as a missing ion. Both of these can be the cause of color centers.

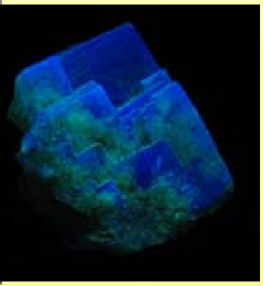
- **If an electron is present at a vacancy, we have an "electron" color center**
  - **Missing anion**
  - **Hypervalent impurity**
- **If an electron is missing from a location where there usually is an electron pair, we have a "hole" color center.**

Many color centers are known, but the exact color causing mechanism has been established in only a very few instances. One of these is the purple "F center" or Frenkel defect of fluorite, one of many types of color center which can form in fluorite. Figure 3A is a two-dimensional representation of the CaF_2 structure. There are several ways by which an F^- ion can be missing from its usual position: this can occur during growth or when energetic radiation displaces an F- ion from its usual position to another point in the crystal; we can also create such centers by growing fluorite in the presence of excess Ca, or by removing some F from a crystal by the application of an electric field.

Fluorite, CaF_2



Purple F-centre:
- **Excess Ca**
- **High energy radiation**
- **Electrical field**



Amethyst

Hole colour centre (Fe^{3+} in SiO_2)

Hole colour centres may be removed by heating
Amethyst: colour changes from violet to yellow
(Yellow citrine quartz)

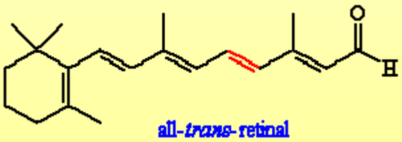
Charge delocalization and molecular orbitals

Chemical bonds have usually excitations in the UV range
Conjugated systems results in delocalization of electrons, and absorptions in the visible spectrum.
HOMO-LUMO transition

In organic materials: The chromophore (Colour bearing) is the part of the molecule that is responsible for the colour.
Auxochromes (Colour enhancers) may change the colour significantly (Electron donating or withdrawing groups)

Acid/base indicators

Photo induced transformations (retinal, cis/trans)



all-*trans*-retinal

Charge transfer

Sapphire

Blue sapphire: Fe^{2+} and Ti^{4+} in Al_2O_3

Adjacent Fe^{2+} and Ti^{4+} gives the colour by photoinduced oxidation/reduction:

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$$

Absorption ca. 2eV, 620nm (yellow)

Fe_3O_4: Also charge transfer

Luminescence

(Light emission from a cool body)

Includes: fluorescence, phosphorescence, chemoluminescence

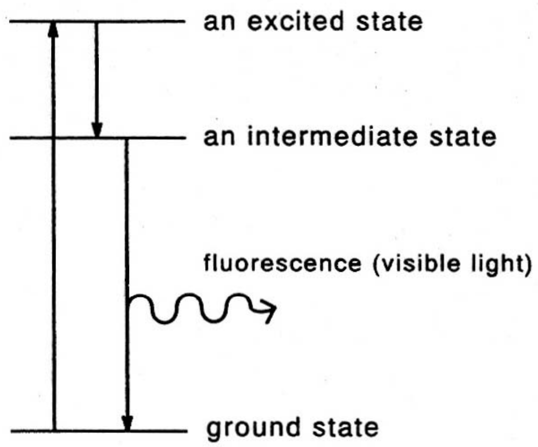
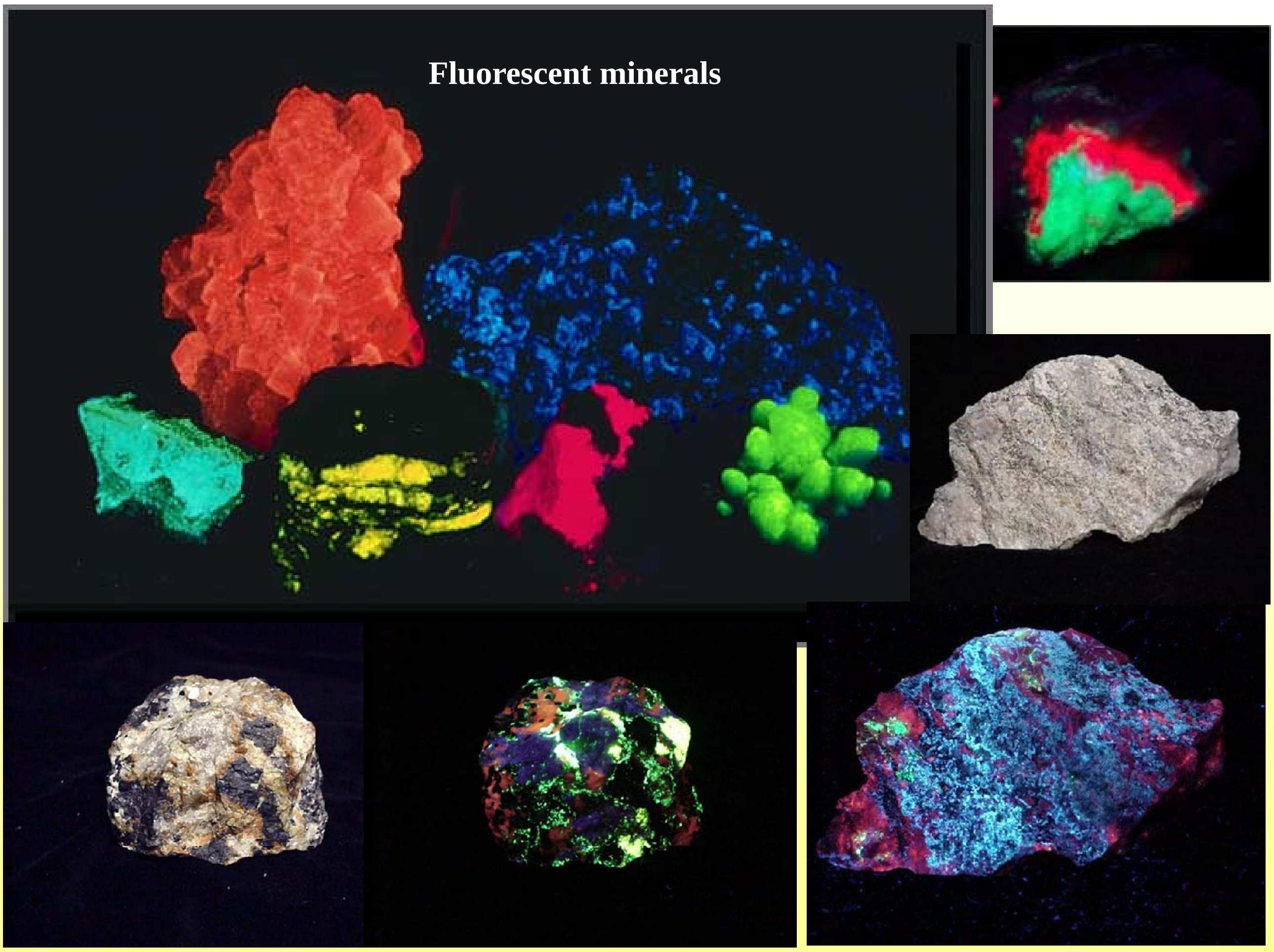


Figure 2.15. Schematic representation of fluorescence.

Lasers (gas and solid state)

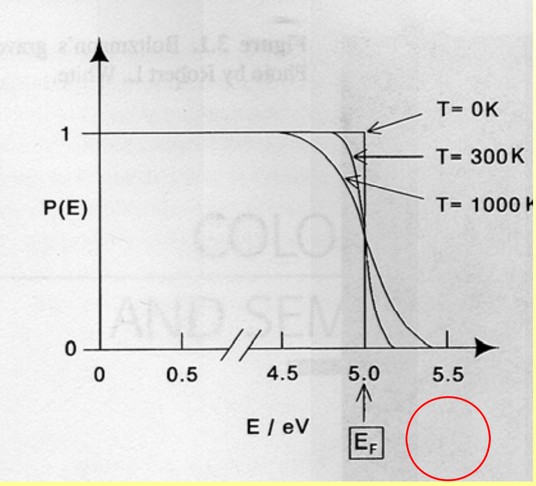
Fluorescent minerals

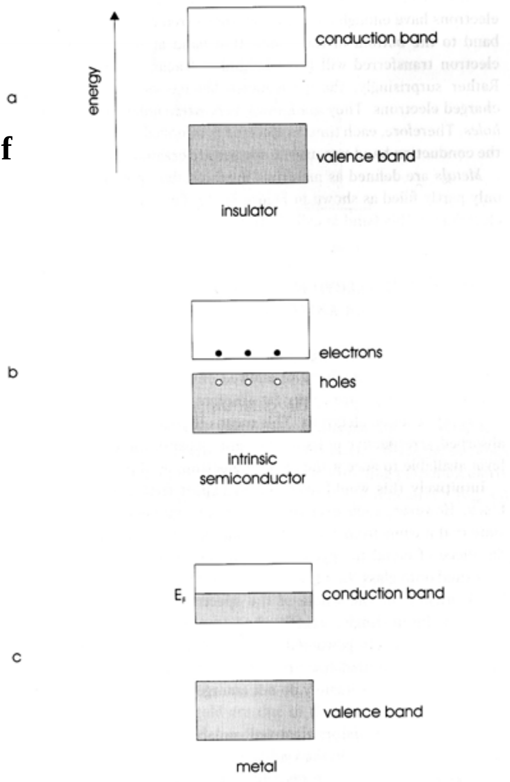


Metals and semiconductors

Best described by band theory

In metals there are a more or less continous band of allowed energies
Metals are often described as “free electron gas”, but also here band structure must be taken into account





igure 10.2 Schematic illustration of the energy bands in (a) an insulator, (b) an ntrinsic semiconductor and (c) a metal. E_F represents the Fermi energy. The bands re idealised and do not show the three-dimensional band geometry which varies with direction in real crystals

From the isolated atom
to band structure.

Large electronic interaction between energy levels: broad bands (e.g. outer electrons of closely spaced large atoms)
Smaller interaction: narrow bands (inner electrons, lager distance between atoms)

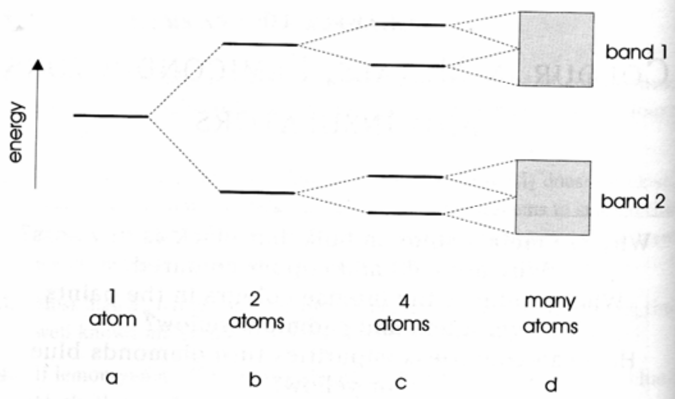
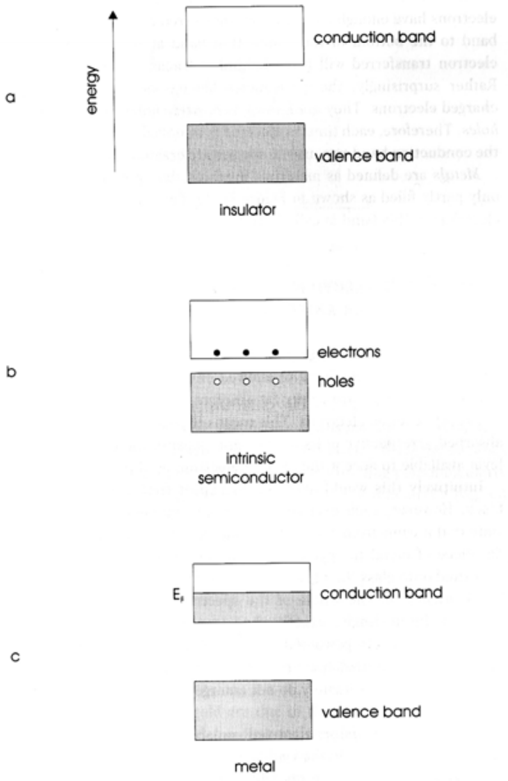


Figure 10.1 The formation of energy bands. (a) Isolated atoms have sharp energy levels. (b) Each energy level in a single atom becomes two energy levels (molecular orbitals) in a diatomic molecule. (c, d) As the number of atoms increases the number of energy levels increases until bands of very closely spaced energy levels form



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Metals

At 0K all energy levels above the Fermi level are empty.

In metals all energies/wavelengths can be absorbed due to the empty levels above the Fermi level.

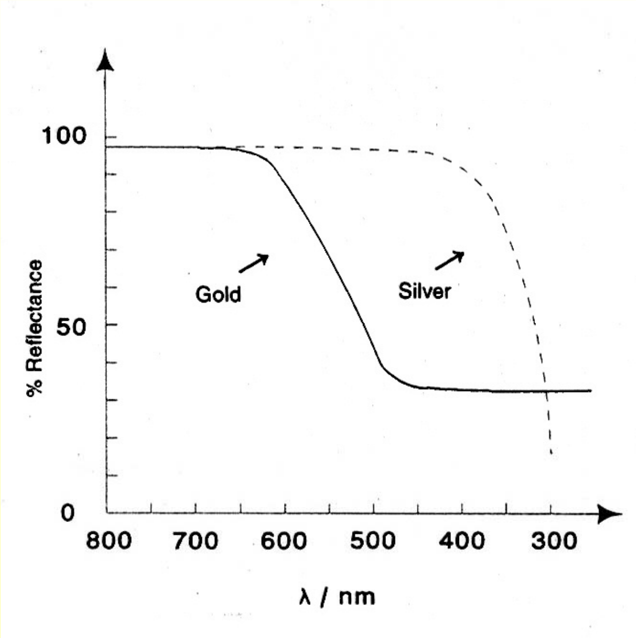
Why, then, are metals not black?

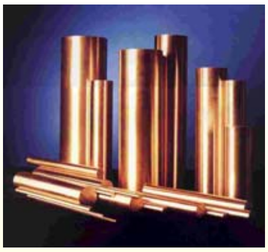
Metals are “shiny” due to an absorption/re-emission process

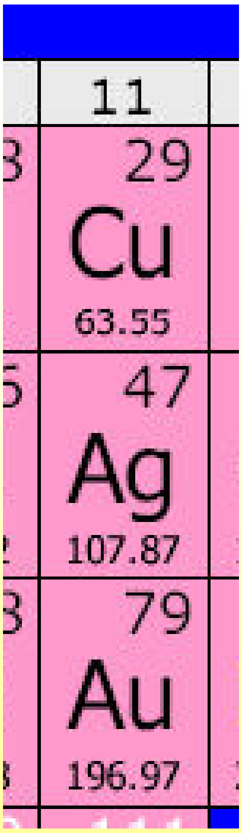
Why is metal powder often black??

Why is gold and copper coloured?

Or rather:
Why is silver not coloured?



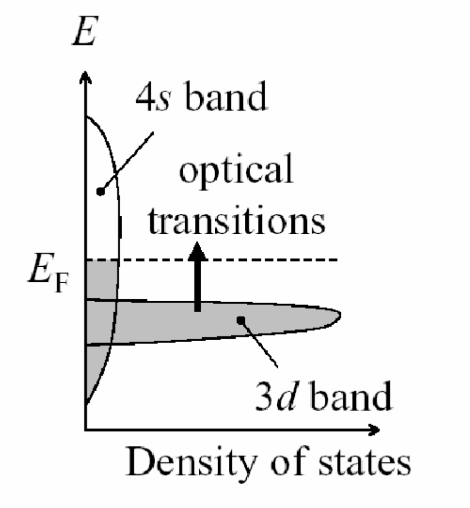


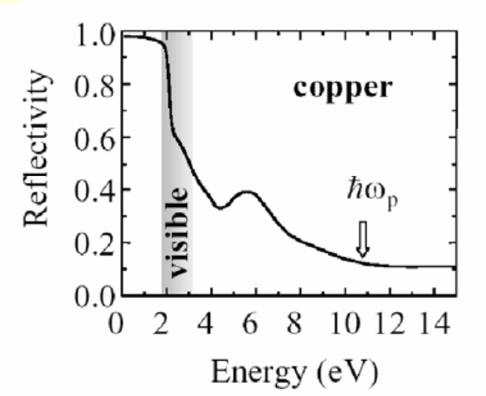

11

29
Cu
63.55

47
Ag
107.87

79
Au
196.97





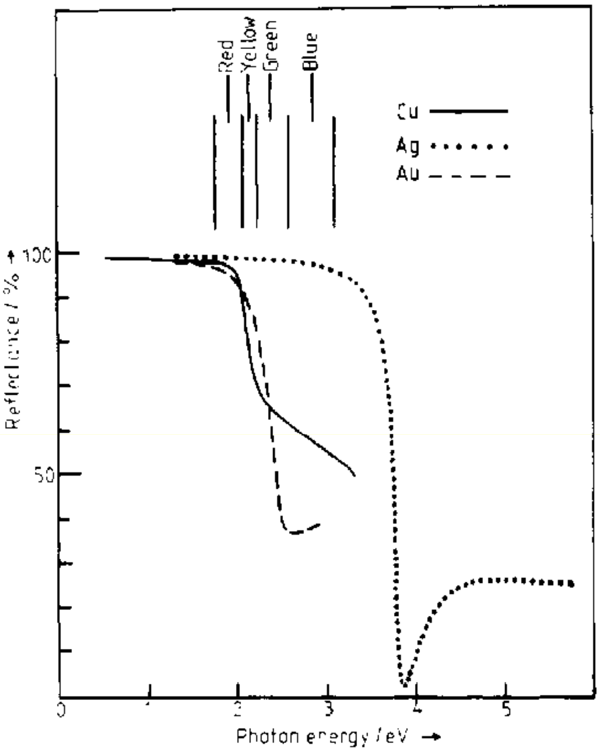


Figure 1 Reflectance curves for Cu, Ag and Au in the visible region. Photon energy ranges corresponding to various coloured visible electromagnetic radiation are shown for comparison

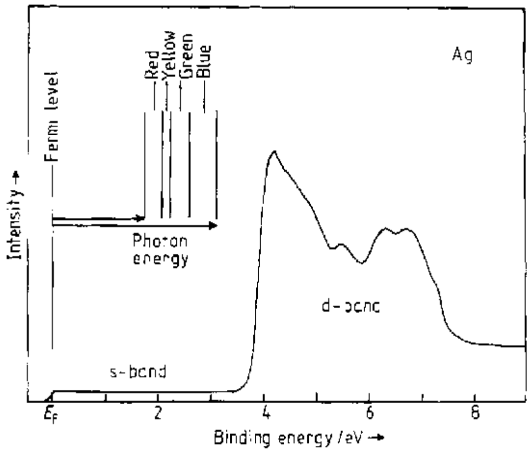


Figure 4 Experimental (Battye *et al* 1977) valence region density of occupied electron states for Ag. Photon energy ranges corresponding to various coloured visible electromagnetic radiation are shown for comparison

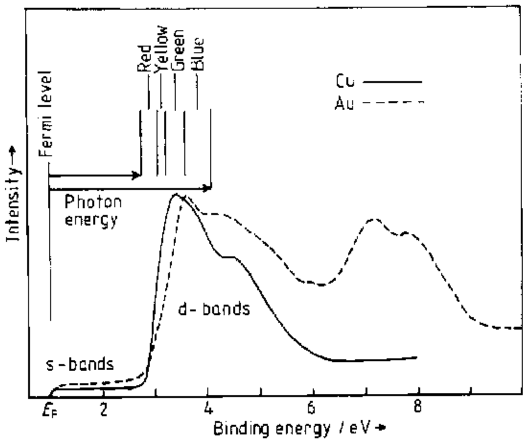


Figure 5 Experimental (Battye *et al* 1977) density of occupied electron states of valence region of Cu and Au. Photon energy ranges corresponding to various coloured visible electromagnetic radiation are shown for comparison

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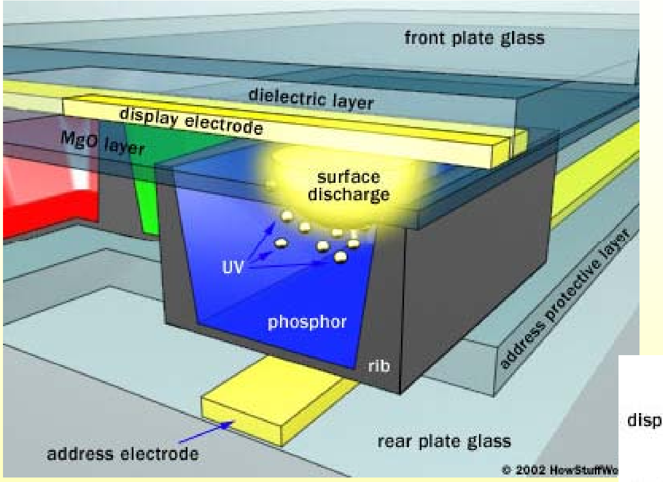
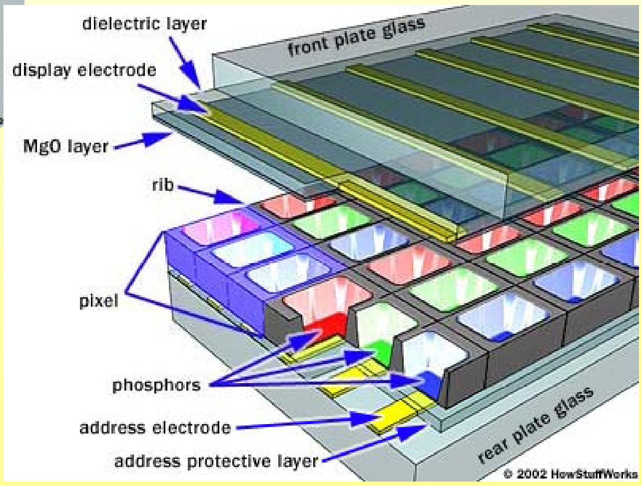
Plasma displays



Xe or Ne gas
TCO electrodes



F-centres in CaF_2

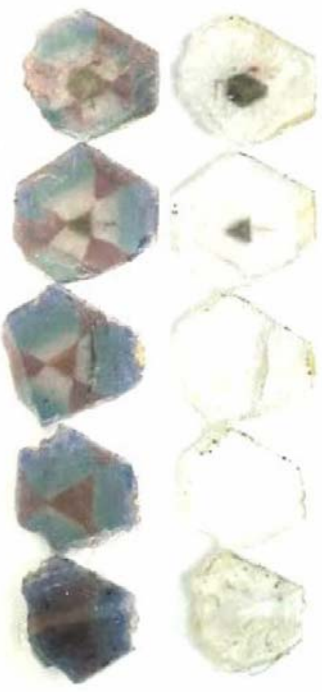
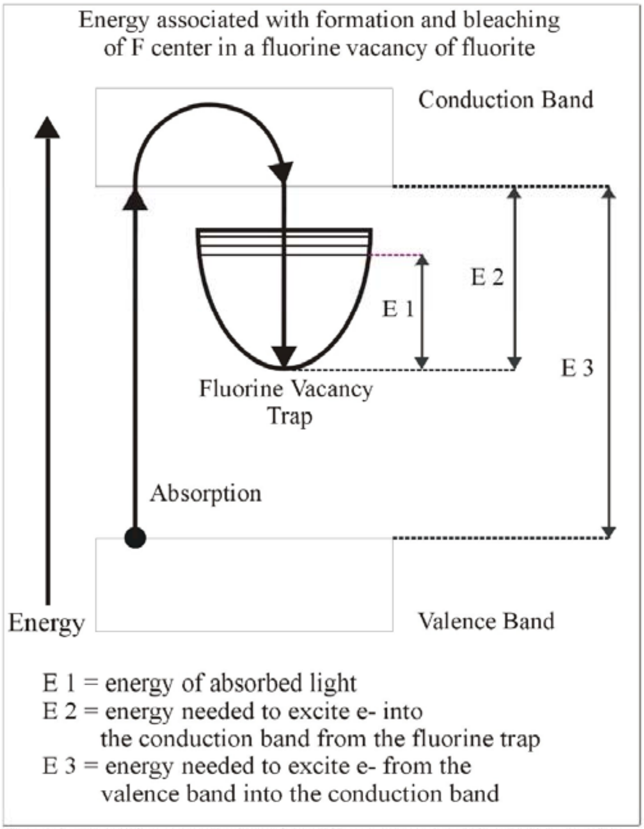


Figure 2. Slices of a single crystal of fluorite from Long Lake, New York. The top row is before irradiation, the bottom row is following irradiation.



Energy associated with formation and bleaching of F center in a fluorine vacancy of fluorite

E 1 = energy of absorbed light
E 2 = energy needed to excite e- into the conduction band from the fluorine trap
E 3 = energy needed to excite e- from the valence band into the conduction band

Figure 3. Schematic energy diagram of the different energy levels involved in creating and destroying an F center, as well as in producing color.

Pure (intrinsic) semiconductors

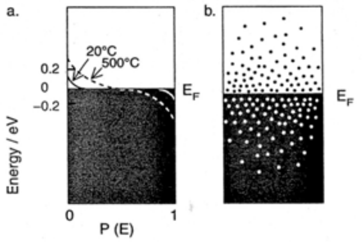


Figure 3.6. Other ways to view the Fermi–Dirac distribution for electrons in a metal: (a) occupational probability, $P(E)$, for energy levels in a typical metal at two different temperatures; (b) occupational probability schematically for $T > 0$ K, with ● representing excited electrons and ○ representing holes.

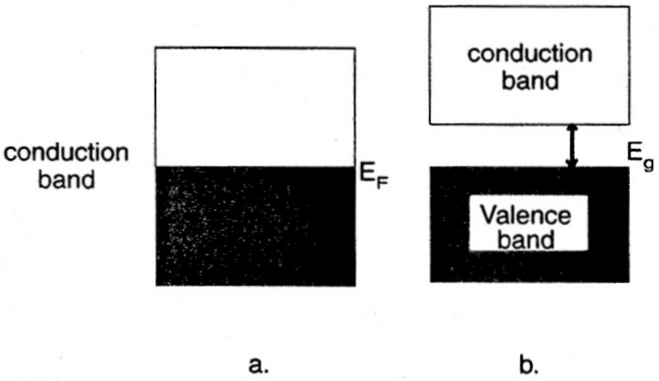


Figure 3.7. Energy bands in (a) a metal and (b) a semiconductor. E_g is the energy gap.

Pure (intrinsic) semiconductors

Element	Lattice parameter/Å	Bond dissociation energy/kJ mol^{-1}	E_g / eV
C (Diamond)	3.57	346	5.4
Si	5.43	222	1.1
Ge	5.66	188	0.66
α – Sn	6.49	146	0.1

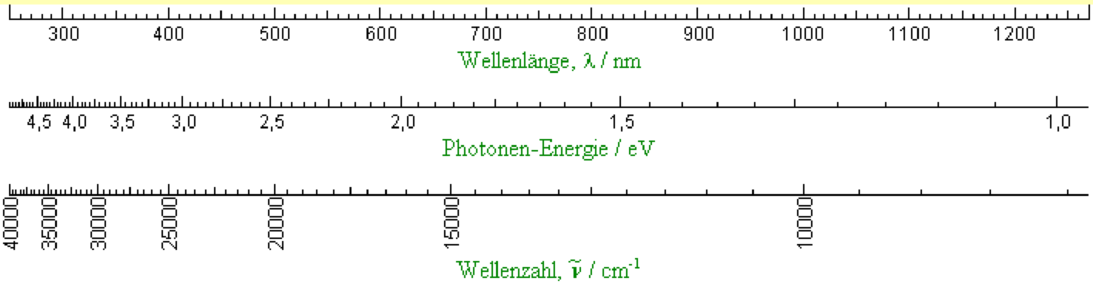
Shorter, stronger bonds result in larger band gap energies.

Pressure or low temperature increase the band gap

The band gap determines the optical properties and colour:

If the band gap is large the material is transparent and colourless (e.g. diamond)
E_g> 3 eV (λ ~ 400 nm)

If the band gap is small, the material may appear either metallic (Si) or black (CdSe) depending on reemission properties
E_g< 1.7 eV (λ ~ 700 nm)



When Eg is in the energy range of visible light, the material absorbs photons with an energy which is higher than the band gap.
1.7 < E_g< 3 eV (λ ~ 400-700 nm)

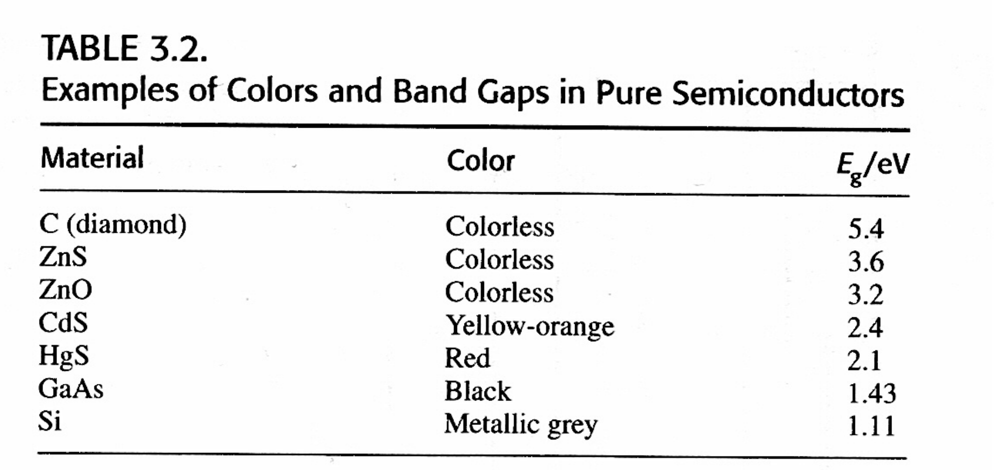
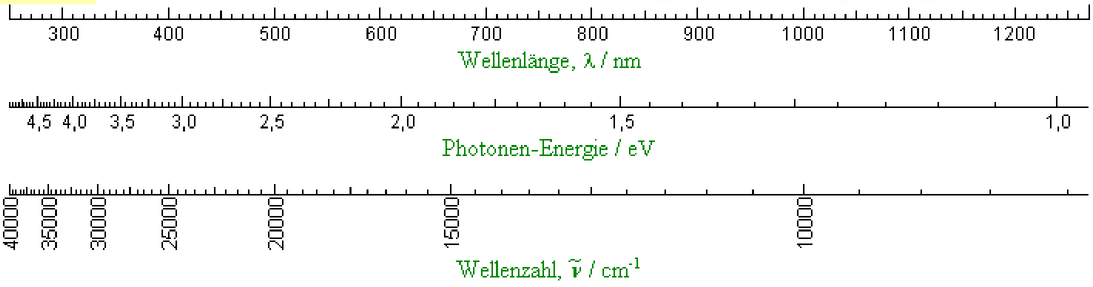


TABLE 3.2.
Examples of Colors and Band Gaps in Pure Semiconductors

Material	Color	E_g/eV
C (diamond)	Colorless	5.4
ZnS	Colorless	3.6
ZnO	Colorless	3.2
CdS	Yellow-orange	2.4
HgS	Red	2.1
GaAs	Black	1.43
Si	Metallic grey	1.11



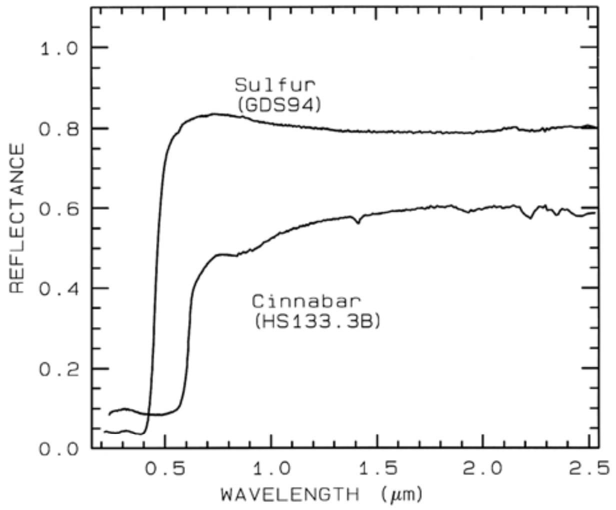
HgS, Cinnabar, Vermilion

Many sulfides are used as pigments

E_g = 2.1 eV (λ = 590 nm)

CdS: Cadmium yellow

As_2S_3: Orpiment



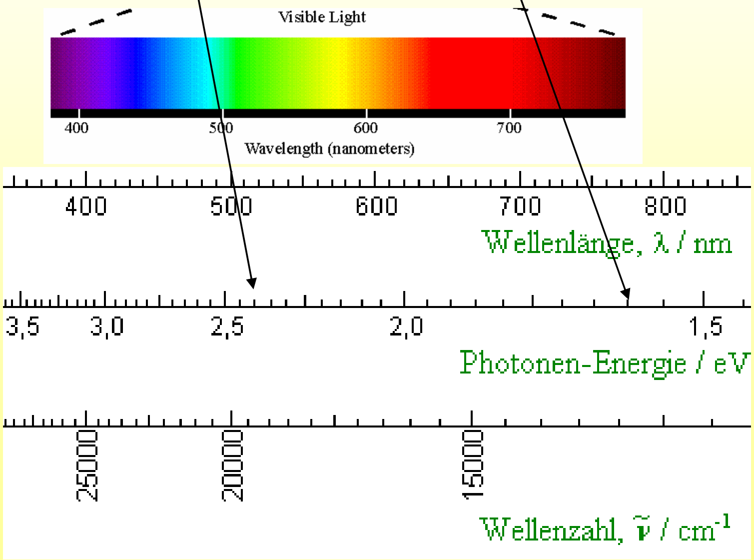
Solid solution: band-gap tuning

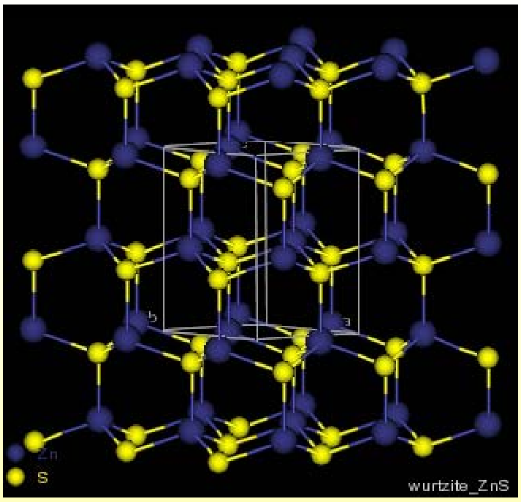
CdS-CdSe

Wurtzite (ZnS) structure

CdS: 2.4 eV,
yellow-orange

CdSe: 1.6 eV,
black





$CdS_{1-x}Se_x$:
colours from yellow (x=0)
through orange and red to black

$CdS_{0.25}Se_{0.75}$: Cadmium orange

$GaP_{1-x}As_x$: LED's and lasers

Doped semiconductors

n-type: The impurity donates electrons to the conduction band
Donor impurity (negative charge carriers)

p-type: The impurity create electron vacancies (holes)
Acceptor impurity (positive charge carriers)

Impurities may create energy levels between the valence and conduction band. This will affect the color of wide band gap semiconductors.

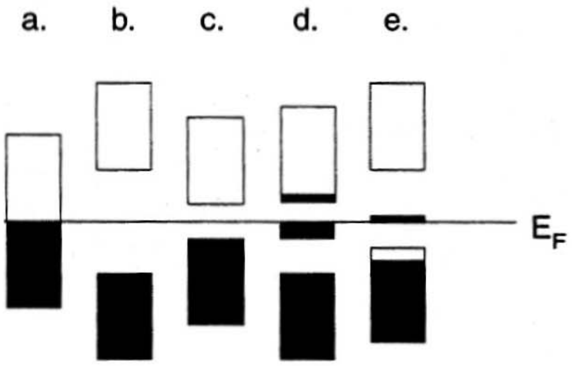


Figure 3.8. Energy bands in (a) a metal, (b) an insulator, (c) a pure semiconductor, (d) an n-type semiconductor, and (e) a p-type semiconductor. E_F is the Fermi energy.

Doped ZnS: phosphorescence

Fluorescence: allowed transition
Phosphorescence: forbidden transition

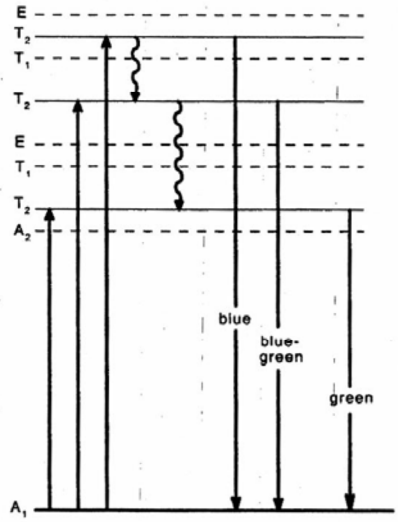
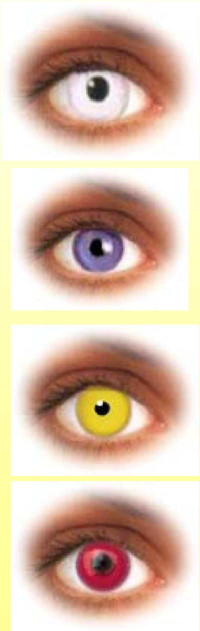
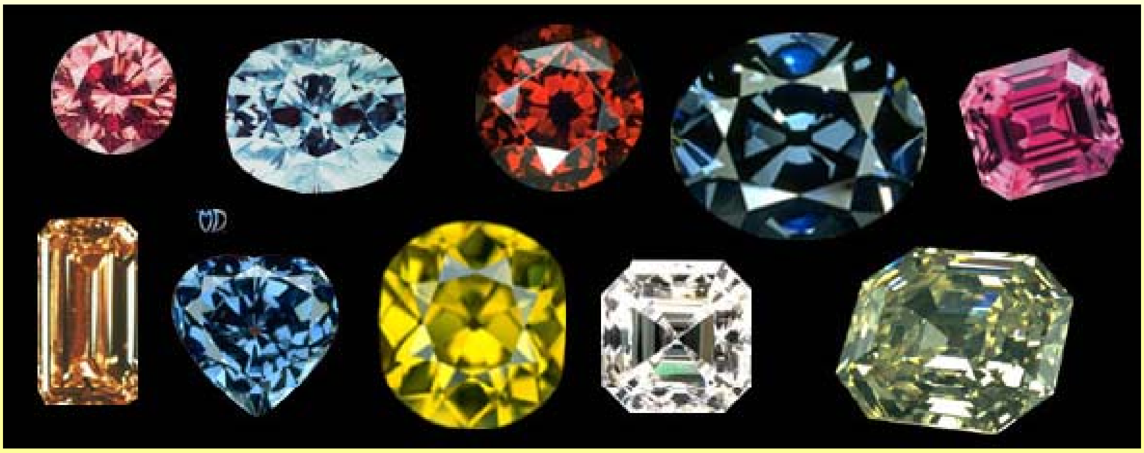


Figure 3.9. Schematic view of phosphorescence due to emission from excited states in the blue phosphor ZnS doped with Ag^+. Adapted from Y. Uehara (1975). *Journal of Chemical Physics*, **62,** 2983.

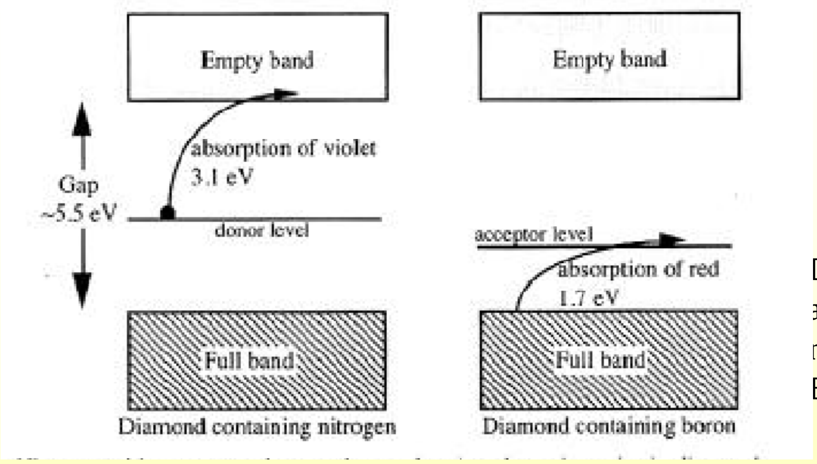
Glow-in-the-dark contact lenses??

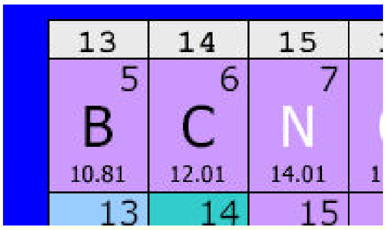


Dirty diamonds, doped semiconductors



C, diamond, doped semiconductors

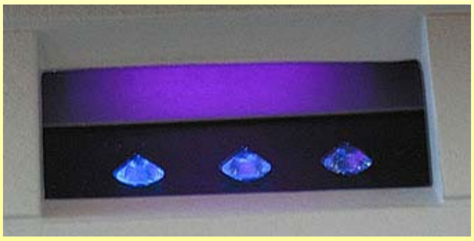




Diamonds doped with small amounts of nitrogen: donor impurity
Boron: acceptor impurity

Blue heart diamond

Hope diamond



Fluorescent diamonds

p-n junctions; LED’s and photovoltaics

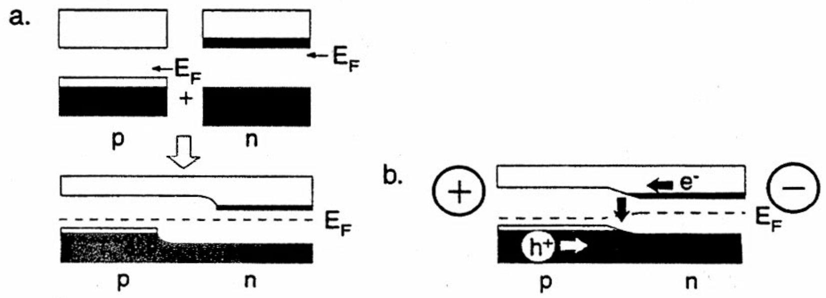
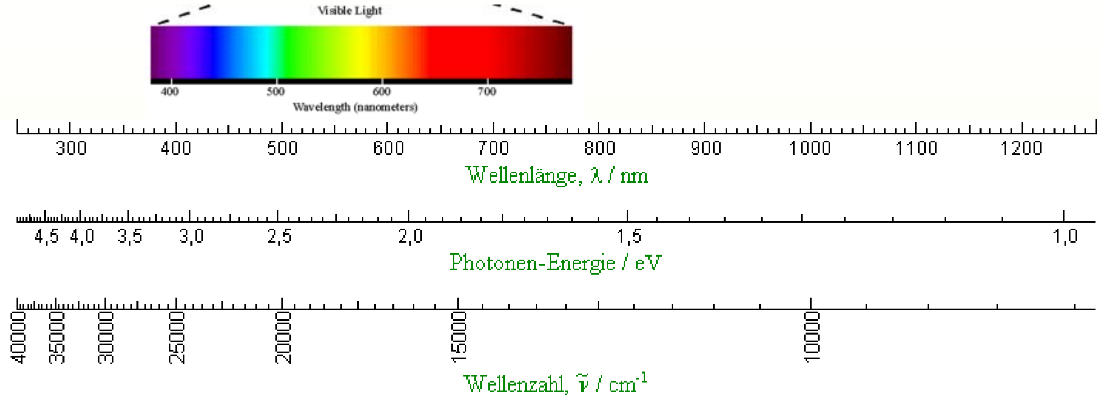
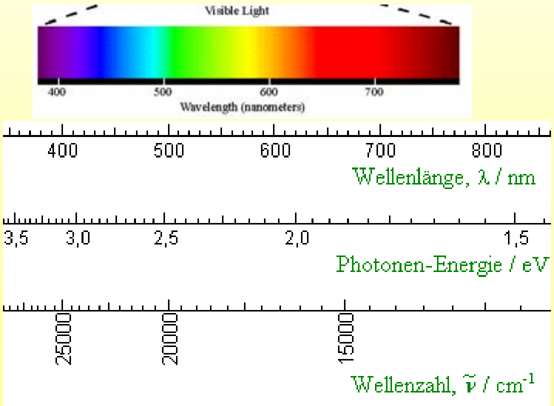


Figure 3.10. The electronic band structure of a p,n-type junction forms a light-emitting diode (LED). (a) When a p-semiconductor is placed beside an n-semiconductor, the Fermi levels become equalized. (For simplicity, the donor and acceptor levels are assumed to be negligible here.) (b) When a field is applied to a p,n-junction, as shown, electrons in the n-conduction band migrate to the positive potential on the p-side, and return to the valence band, recombining with the holes in the p-semiconductor. Similarly, the holes in the p-semiconductor migrate toward the negative n-side and recombine with electrons. The electrons dropping from the conduction band to the valence band emit light corresponding to the energy of the band gap. For example, the emission from $GaAs_{0.6}P_{0.4}$ is red.

Image of fluorescence in various sized Cadmium Selenide Quantum Dots.

(Dr. D. Talapin, University of Hamburg, http://www.chemie.uni-hamburg.de/pc/Weller/). Specific permission to use this image has been granted from Andrey Rogach - Lehrstuhl für Photonik und Optoelektronik Department für Physik und CeNS Ludwig-Maximilians-Universtität München.


Visible Light
400
500
600
700
Wavelength (nanometers)
300
400
500
600
700
800
900
1000
1100
1200
Wellenlänge, λ / nm
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
Photonen-Energie / eV
40000
35000
30000
25000
20000
15000
10000
Wellenzahl, $\tilde{\nu}$ / cm^{-1}


Visible Light
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Wavelength (nanometers)
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Wellenlänge, λ / nm
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2,0
1,5
Photonen-Energie / eV
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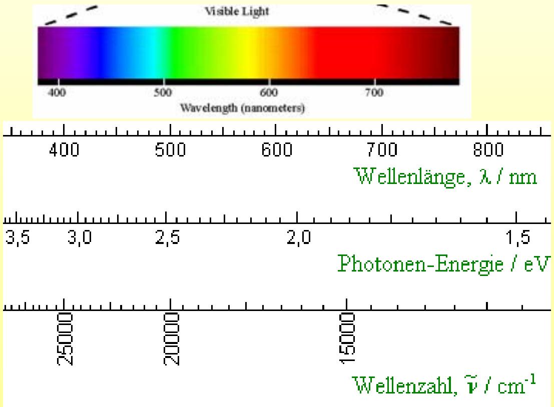
15000
Wellenzahl, $\tilde{\nu}$ / cm^{-1}


Visible Light
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Wavelength (nanometers)
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Wellenlänge, λ / nm
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2,0
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Photonen-Energie / eV
25000
20000
15000
Wellenzahl, $\tilde{\nu}$ / cm^{-1}