# **Color in materials**



KJM3100 V2007

## Pigments







#### Triboluminescence





KJM3100 V2007







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. KJM3100 V2007

#### **Interference colours**







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)



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



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. KJM3100 V2007

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**

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		



Energy in electronic energy levels, vibrational and rotational energy levels.  $500 \text{ nm} = 20000 \text{ cm}^{-1}$ 

Energy transitions involving valence electrons may be in the visible spectrum Energy transitions involving closed shell electrons are in the UV/X-ray region



#### **Transmission/reflection**

The absorbed and transmitted colours are complementary



## 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.

















Azurite, Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>

Malachite, Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>



**Rhodochrosite**, Mn(CO<sub>3</sub>)

KJM3100 V2007

#### **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<sup>-</sup> 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.



#### Amethyst

Hole colour centre (Fe<sup>3+</sup> in SiO<sub>2</sub>)

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



![](_page_17_Picture_4.jpeg)

KJM3100 V2007

#### 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)

![](_page_17_Figure_12.jpeg)

#### **Charge transfer**

Sapphire Blue sapphire: Fe<sup>2+</sup> and Ti<sup>4+</sup> in Al<sub>2</sub>O<sub>3</sub> Adjacent Fe<sup>2+</sup> and Ti<sup>4+</sup> gives the colour by photoinduced oxidation/reduction: Fe<sup>2+</sup> + Ti<sup>4+</sup> → Fe<sup>3+</sup> + Ti<sup>3+</sup> Absorption ca. 2eV, 620nm (yellow)

Fe<sub>3</sub>O<sub>4</sub>: Also charge transfer

![](_page_18_Picture_3.jpeg)

![](_page_18_Picture_4.jpeg)

![](_page_18_Figure_6.jpeg)

![](_page_19_Picture_0.jpeg)

![](_page_19_Figure_1.jpeg)

![](_page_19_Figure_2.jpeg)

Figure 10.2 Schematic illustration of the energy bands in (a) an insulator, (b) an ntrinsic semiconductor and (c) a metal. E<sub>r</sub> represents the Fermi energy. The bands ire idealised and do not show the three-dimensional band geometry which varies with direction in real crystals

с

KJM3100 V2007

# 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)

![](_page_20_Figure_2.jpeg)

![](_page_20_Figure_3.jpeg)

a

b

С

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

KJM3100 V2007

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

#### 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??

![](_page_20_Picture_13.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_22_Figure_0.jpeg)

**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

![](_page_22_Figure_2.jpeg)

**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

![](_page_22_Figure_5.jpeg)

![](_page_23_Figure_0.jpeg)

#### Pure (intrinsic) semiconductors

	Element	Lattice parameter/Å	Bond dissociation energy/kJ mol <sup>-1</sup>	${ m E_g}/eV$	
Shorter, stronger bonds result in	C (Diamond)	3.57	346	5.4	
larger band gap energies.	Si	5.43	222	1.1	
Pressure or low temperature	Ge	5.66	188	0.66	
increase the band gap	$\alpha - Sn$	6.49	146	0.1	

The band gap determines the optical properties and colour:

If the band gap is large the material is transparent and colourless (e.g. diamond)  $E_{\rm o}{>}~3~eV~(\lambda\sim400~nm)$ 

If the band gap is small, the material may appear either metallic (Si) or black (CdSe) depending on reemission properties

![](_page_24_Figure_5.jpeg)

When Eg is in the energy range of visible light, the material absorbs photons with an energy which is higher than the band gap.  $1.7 < E_g < 3 \text{ eV} (\lambda \sim 400-700 \text{ nm})$ 

#### TABLE 3.2.

Examples of Colors and Band Gaps in Pure Semiconductors

		Material			Color Colorless Colorless			E <sub>g</sub> /eV		
		C (diamond) ZnS ZnO CdS HgS		5.4						
				3.6						
					Colorless Yellow-orange Red			3.2 2.4 2.1		
		GaAs				Black			1	.43
		Si				Metallic g	rey		1	.11
	1 1									
	300	400	500	600	700 Wellenli	800 änge, λ / nm	900	1000	1100	1200
	ատասհատաստում 4,5 4,0	3,5 3,0	2,5	<u>,,,,,</u> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Photonen	1,5 -Energie / eV				<u> </u>
	35000	1	<u>-</u> 5000		15000-			10000-		
KJM3100 V2007					Wellenz	ahi, ν/cm <sup>*</sup>				

#### HgS, Cinnabar, Vermilion

![](_page_25_Figure_1.jpeg)

#### **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.

![](_page_26_Figure_4.jpeg)

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.  $E_{\rm F}$  is the Fermi energy.

#### **Doped ZnS: phosphorescence**

![](_page_26_Picture_7.jpeg)

**Glow-in-the-dark** 

Fluorescence: allowed transition Phosphorescence: forbidden transition

![](_page_26_Figure_9.jpeg)

Figure 3.9. Schematic view of phosphorescence due to emission from excited states in the blue phosphor ZnS doped with Ag<sup>+</sup>. Adapted on Y. Uehara (1975). *Journal* of Chemical Physics, 62, 283.

![](_page_26_Picture_11.jpeg)

![](_page_26_Picture_12.jpeg)

![](_page_26_Picture_13.jpeg)

![](_page_26_Picture_14.jpeg)

#### Dirty diamonds, doped semiconductors

![](_page_27_Picture_1.jpeg)

#### p-n junctions; LED's and photovoltaics

![](_page_28_Figure_1.jpeg)

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<sub>0.6</sub>P<sub>0.4</sub> is red.

KJM3100 V2007

![](_page_28_Picture_4.jpeg)

Image of fluorescence in various sized Cadmium Selenide Quantum Dots.

(Dr. D. Talapin, University of Hamburg, http://www.chemie.unihamburg.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.

![](_page_29_Figure_0.jpeg)