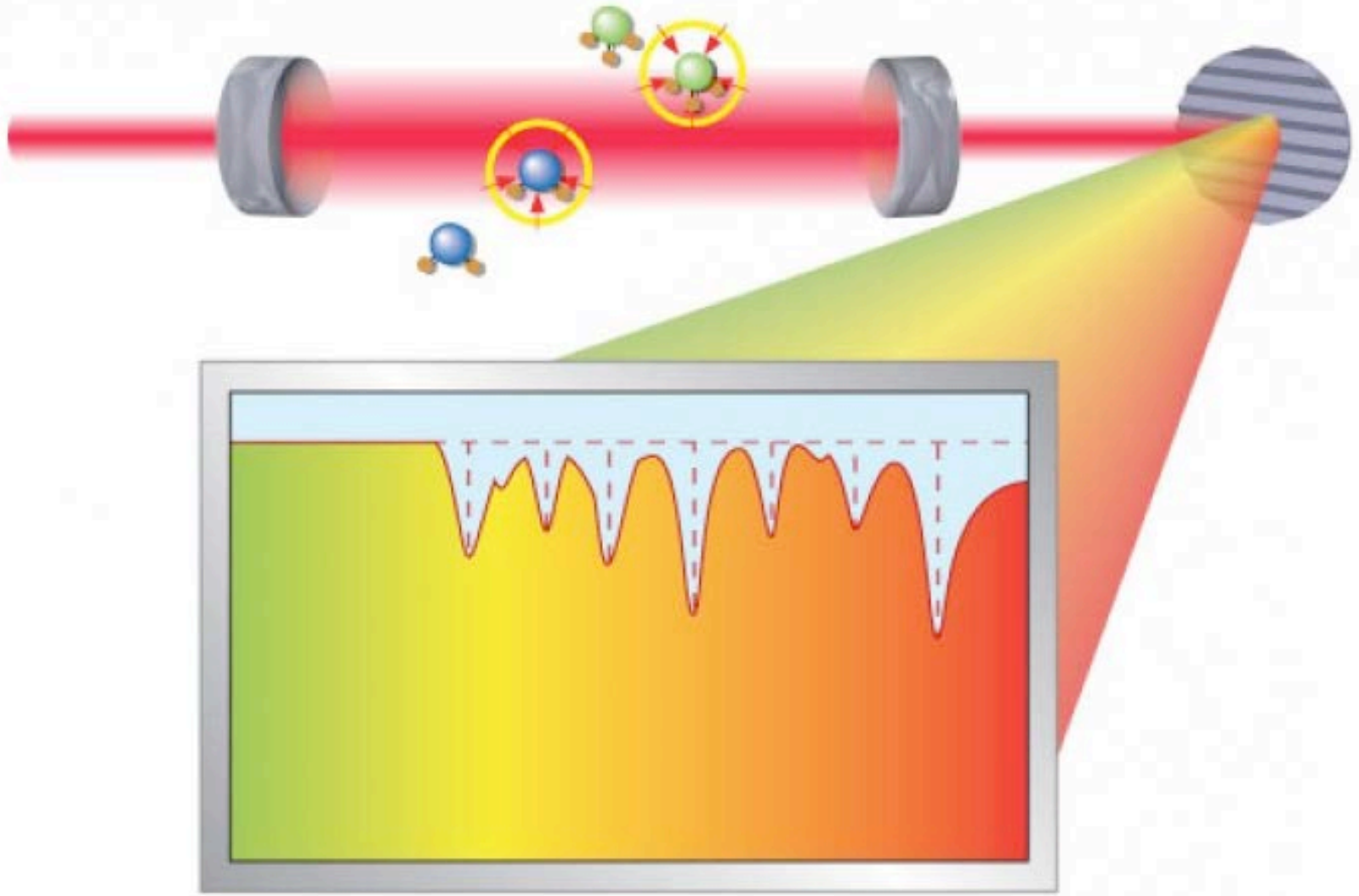


Spectroscopy: The Study of Squiggly Lines



Reflectance spectroscopy: light absorbed at specific wavelengths corresponding to energy level transitions

Interaction of Radiant Energy and Matter

What causes absorption features in visible & infrared spectra?

- 1) Rotational absorption (gases)**
- 2) Electronic absorption**
- 3) Vibrational absorption**

Rotational Processes

Photons striking *free* molecules can cause them to rotate. The rotational states are quantized, so there are discrete photon energies that, when absorbed, cause the molecules to spin.

Rotational interactions are low-energy interactions and the absorption features are at long infrared wavelengths.

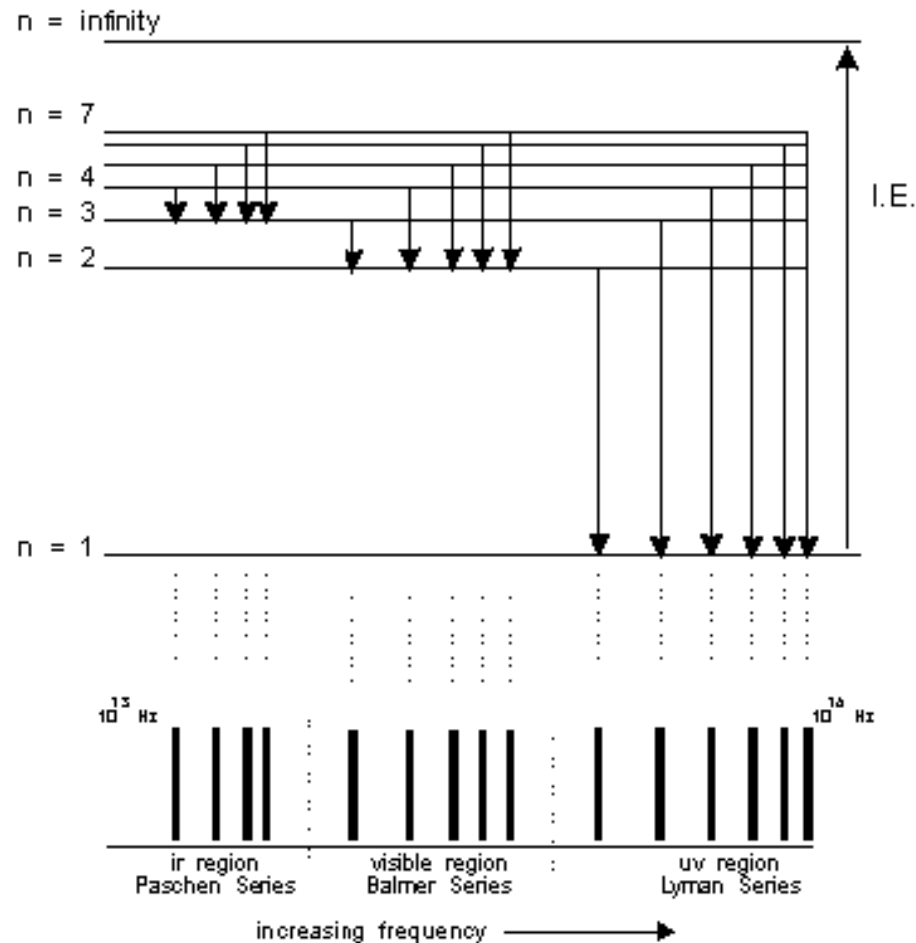
Not important in remote sensing of solid materials

Electronic Processes

Isolated atoms and ions have discrete energy states. Absorption of photons of a specific wavelength causes a change from one energy state to a higher one.

Four types:

- Crystal Field Effects
- Charge Transfer Absorptions
- Conduction Bands
- Color Centers

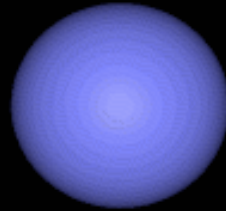


Electronic Processes

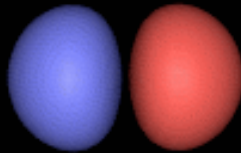
Crystal Field Effects

The electronic energy levels of an isolated ion are usually split and displaced when located in a solid. Unfilled d orbitals are split by interaction with surrounding ions and assume new energy values. These new energy values (transitions between them and consequently their spectra) are primarily determined by the valence state of the ion (Fe^{2+} , Fe^{3+}), coordination number, and site symmetry.

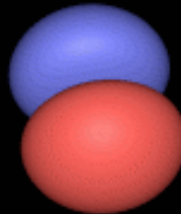
Electron Orbits



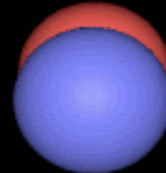
s



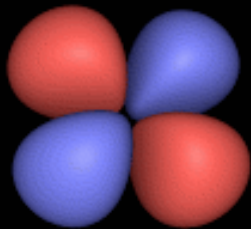
p_x



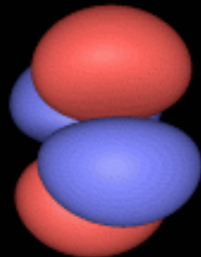
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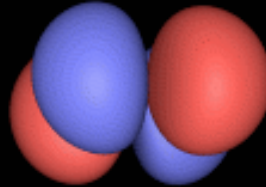
p_z



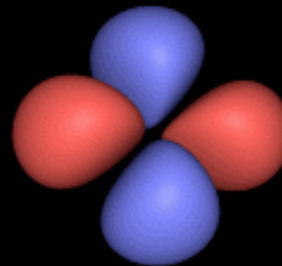
d_{xy}



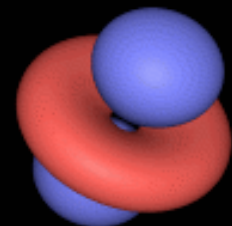
d_{xz}



d_{yz}



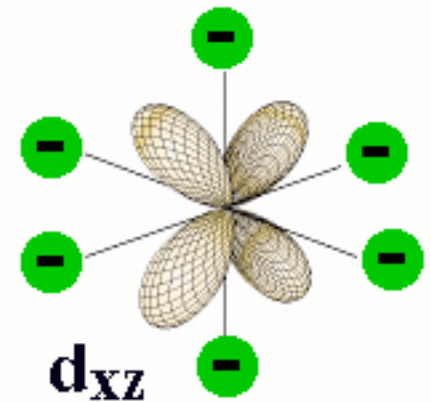
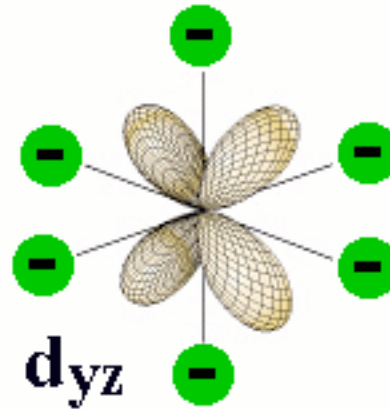
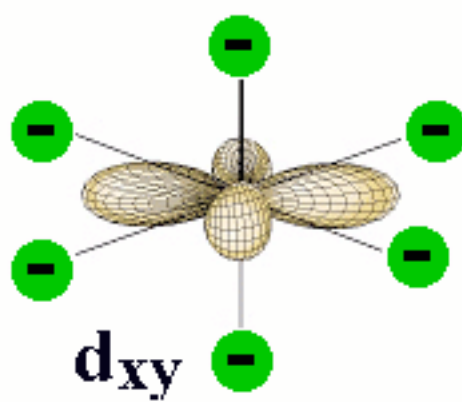
d_{x² - y²}



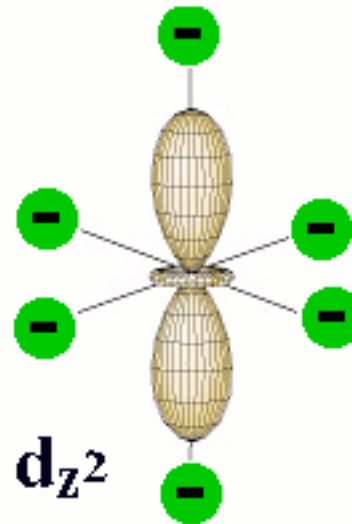
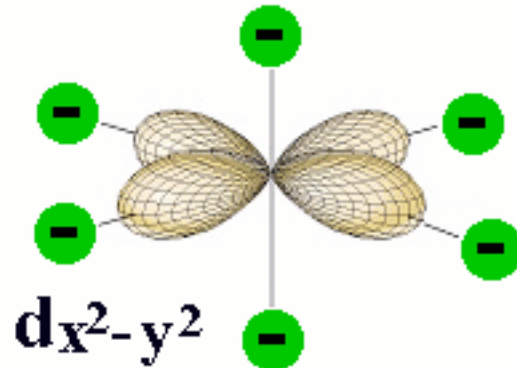
d_{z²}

Energy Level Splitting in Solids: Part 1

**Lower
Energy
Levels**

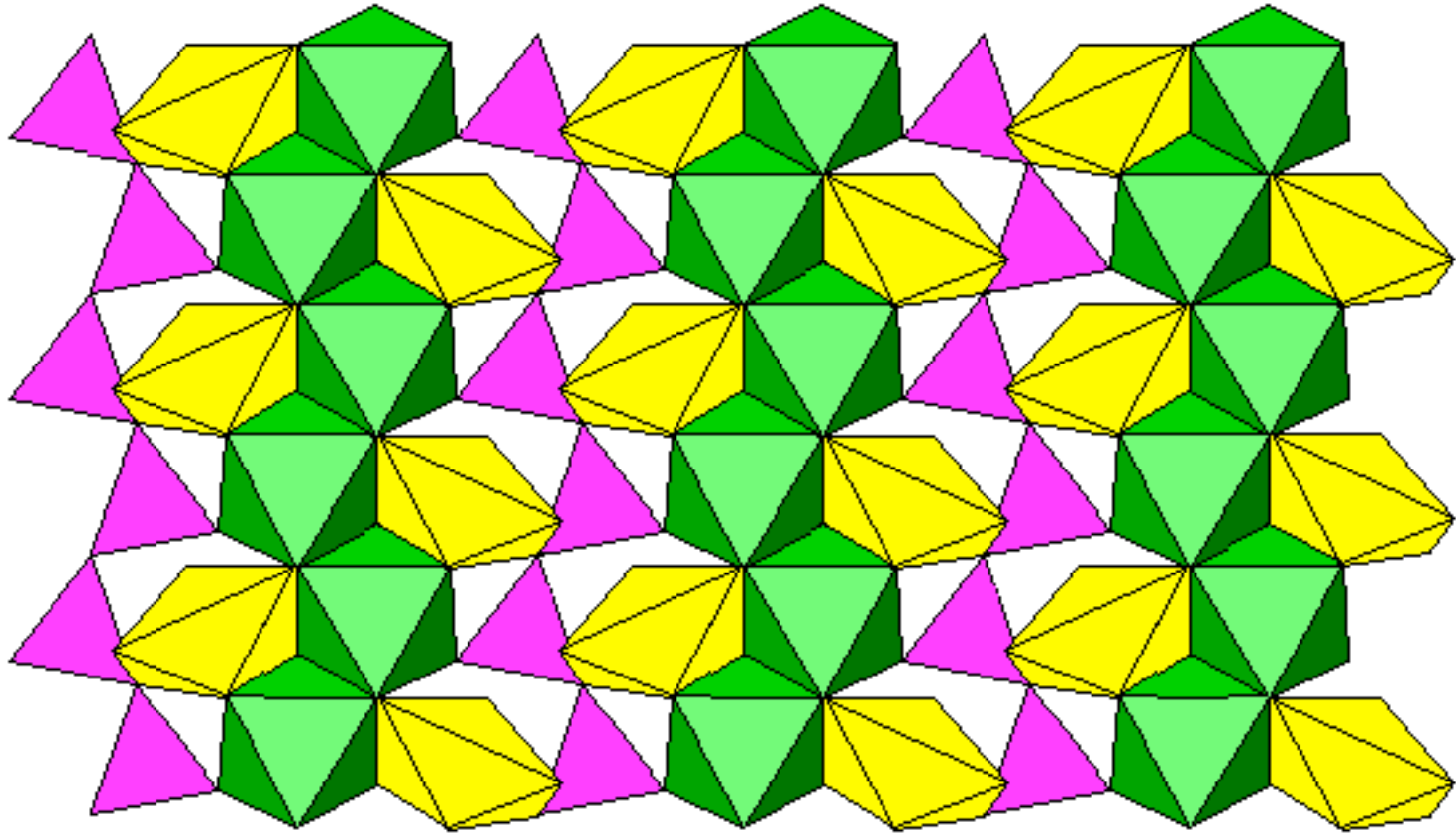


**Higher
Energy
Levels**



In a free atom these have equal energy, but not in a crystal...

Energy Level Splitting in Solids: Part 2



Distortion of some “sites” in a crystal → further energy splitting
→ *diagnostic of mineralogy*

Unfilled *d* orbitals: the transition metals

Periodic Table of the Elements

1 1 H Hydrogen 1.00784	2 4 He Helium 4.002602											13 5 B Boron 10.811	14 6 C Carbon 12.0107	15 7 N Nitrogen 14.00644	16 8 O Oxygen 15.9994	17 9 F Fluorine 18.9984032	18 10 Ne Neon 20.1797				
3 3 Li Lithium 6.941	4 4 Be Beryllium 9.012182											13 13 Al Aluminum 26.981538	14 14 Si Silicon 28.0855	15 15 P Phosphorus 30.973761	16 16 S Sulfur 32.066	17 17 Cl Chlorine 35.453	18 18 Ar Argon 39.948				
11 3 Na Sodium 22.989770	12 4 Mg Magnesium 24.3050	3 21 Sc Scandium 44.955910	4 22 Ti Titanium 47.867	5 23 V Vanadium 50.9415	6 24 Cr Chromium 51.9961	7 25 Mn Manganese 54.938049	8 26 Fe Iron 55.8457	9 27 Co Cobalt 58.933200	10 28 Ni Nickel 58.6934	11 29 Cu Copper 63.546	12 30 Zn Zinc 65.409	13 31 Ga Gallium 69.723	14 32 Ge Germanium 72.64	15 33 As Arsenic 74.92160	16 34 Se Selenium 78.96	17 35 Br Bromine 79.904	18 36 Kr Krypton 83.798				
19 5 K Potassium 39.0983	20 4 Ca Calcium 40.078	39 39 Y Yttrium 88.90585	40 40 Zr Zirconium 91.224	41 41 Nb Niobium 92.90638	42 42 Mo Molybdenum 95.94	43 43 Tc Technetium (98)	44 44 Ru Ruthenium 101.07	45 45 Rh Rhodium 102.90550	46 46 Pd Palladium 106.42	47 47 Ag Silver 107.8682	48 48 Cd Cadmium 112.411	49 49 In Indium 114.818	50 50 Sn Tin 118.710	51 51 Sb Antimony 121.760	52 52 Te Tellurium 127.60	53 53 I Iodine 126.90447	54 54 Xe Xenon 131.293				
37 5 Rb Rubidium 85.4678	38 4 Sr Strontium 87.62											81 81 Tl Thallium 204.3833	82 82 Pb Lead 207.2	83 83 Bi Bismuth 208.98038	84 84 Po Polonium (209)	85 85 At Astatine (210)	86 86 Rn Radon (222)				
55 6 Cs Cesium 132.90545	56 4 Ba Barium 137.327											113 113 Uut Ununtrium (284)	114 114 Uuq Ununquadium (289)	115 115 Uup Ununpentium (288)	116 116 Uuh Ununhexium (292)	117 117 Uus Ununseptium	118 118 Uuo Ununoctium				
87 7 Fr Francium (223)	88 4 Ra Radium (226)																				

- Alkali metals
- Alkaline earth metals
- Transition metals
- Lanthanide series
- Actinide series
- Poor metals
- Nonmetals
- Noble gases

- C Solid
- Br Liquid
- H Gas
- Tc Synthetic

Atomic masses in parentheses are those of the most stable or common isotope.

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Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

57 La Lanthanum 138.9055	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

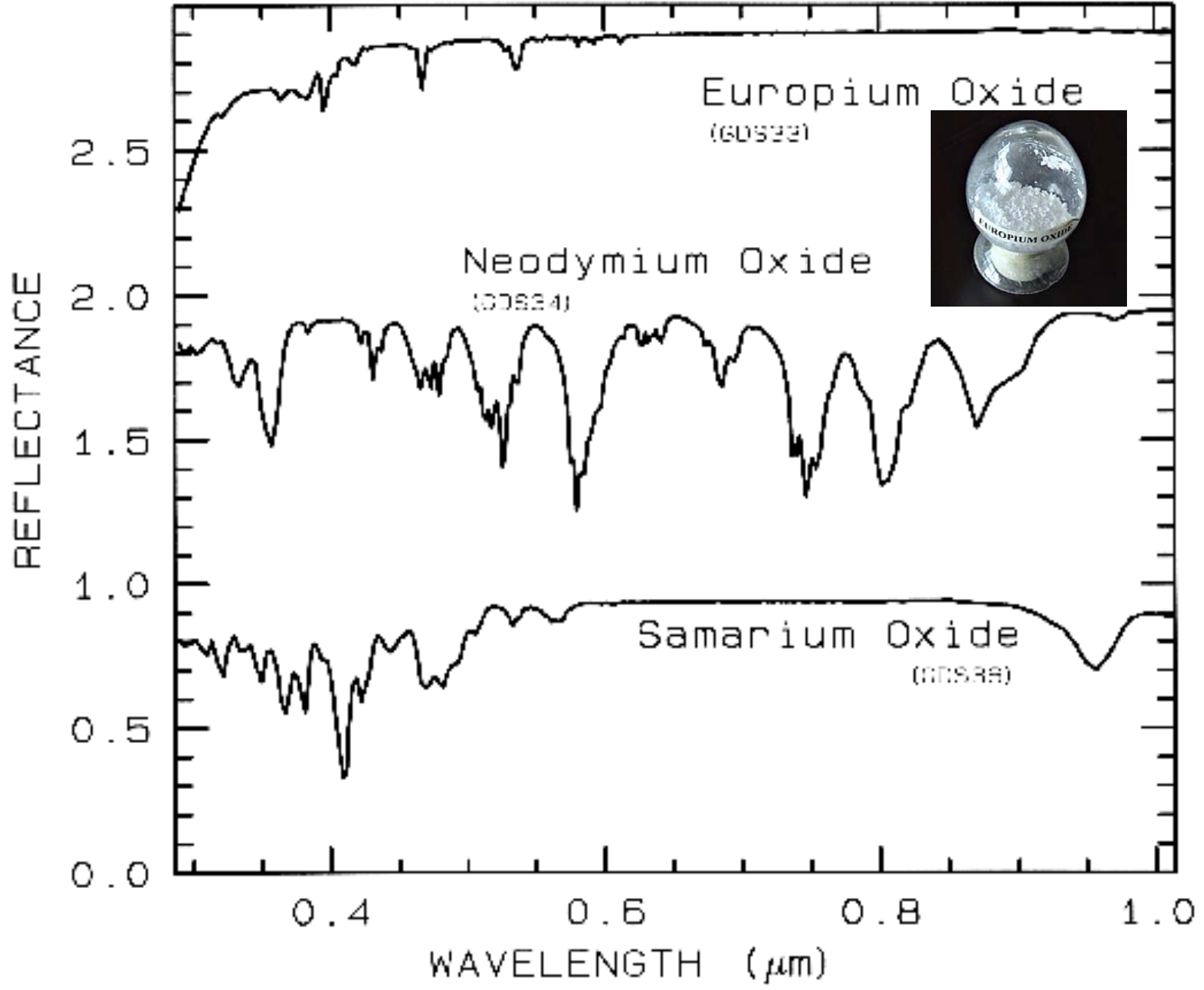
Iron is the most geologically abundant transition metal

Electronic Processes

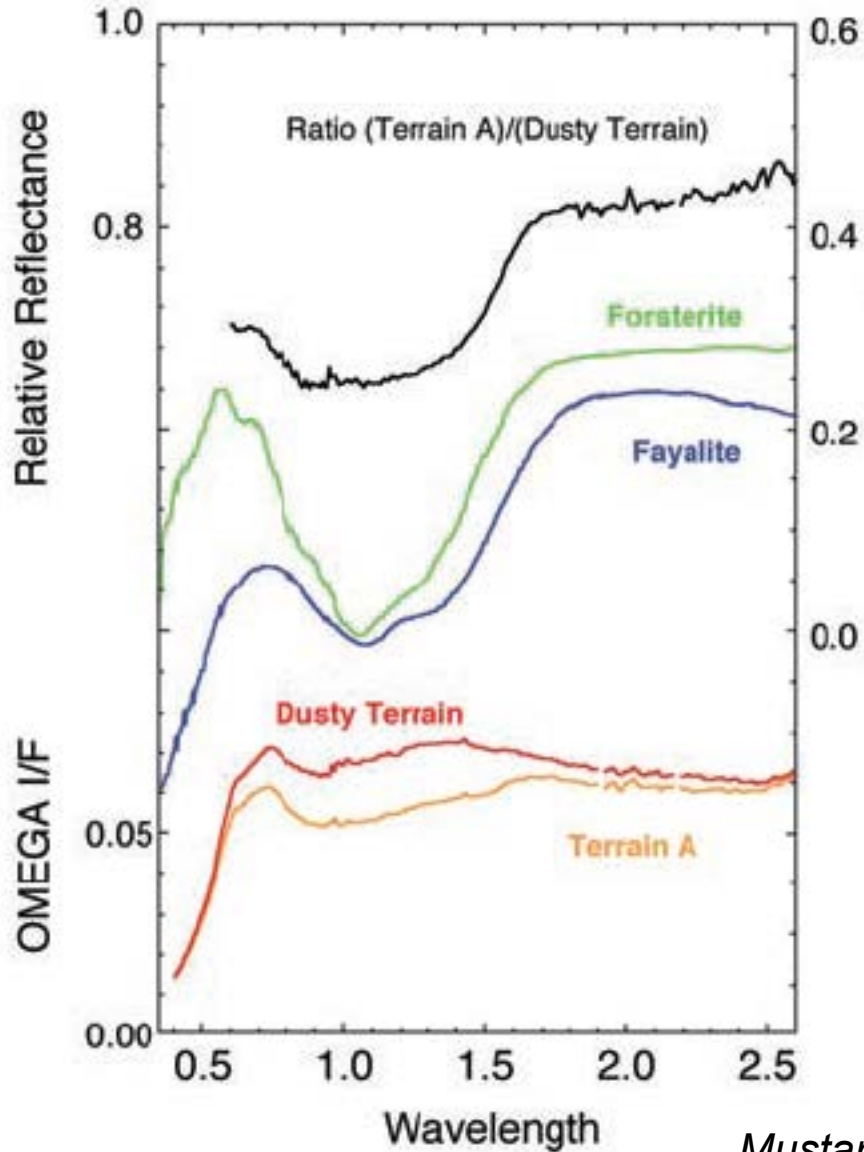
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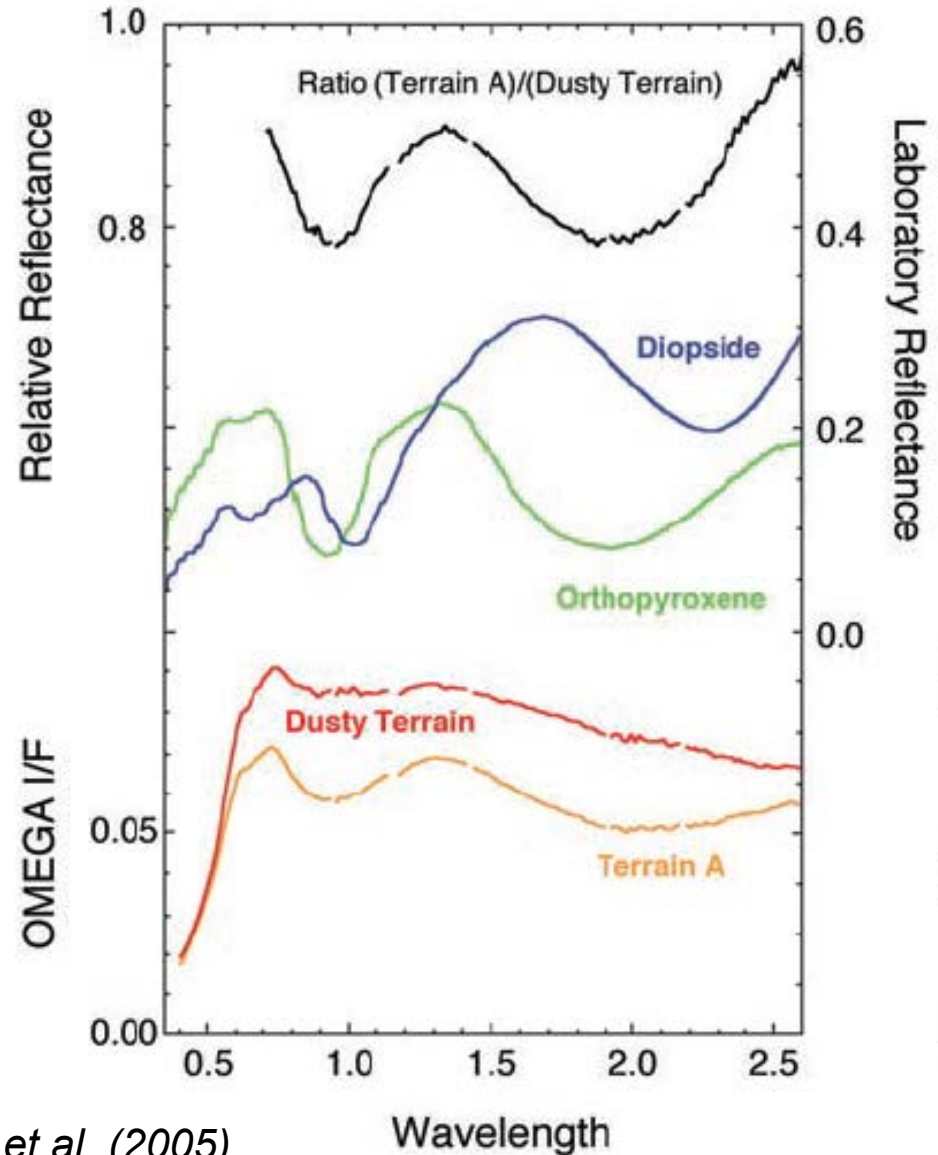
Electronic transitions, crystal field effects



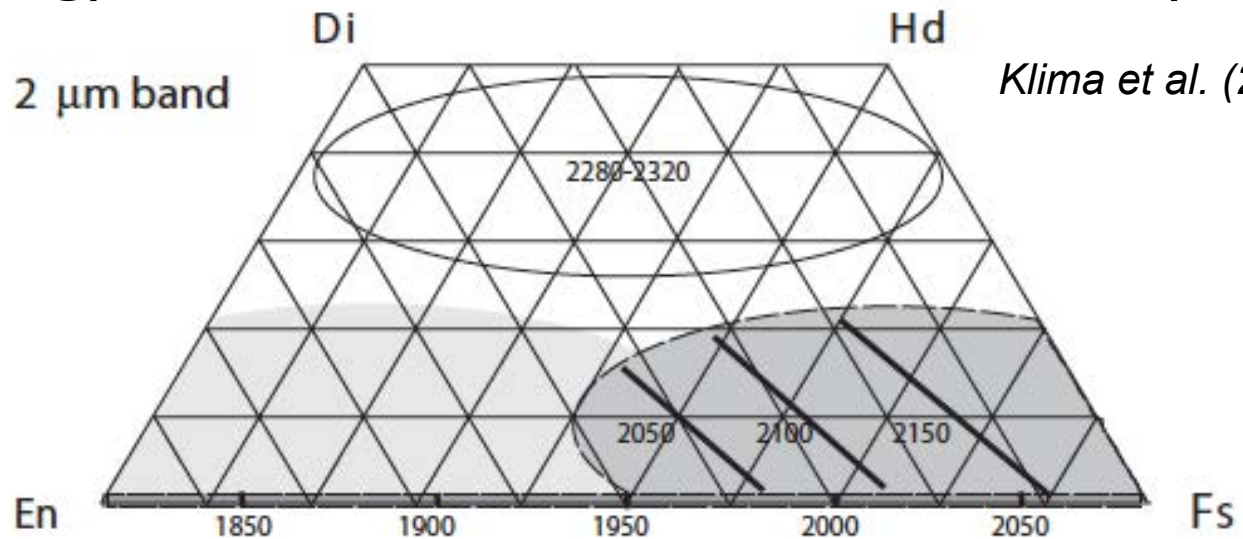
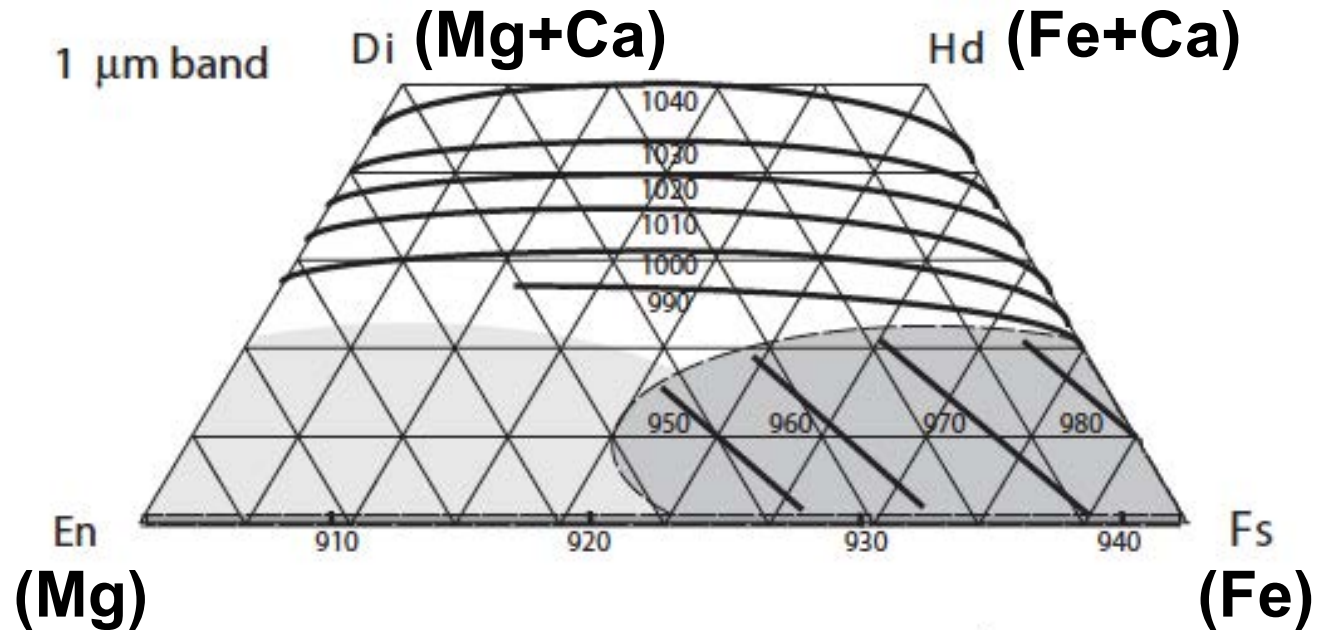
Fe electronic transitions in olivine, pyroxene



Mustard et al. (2005)

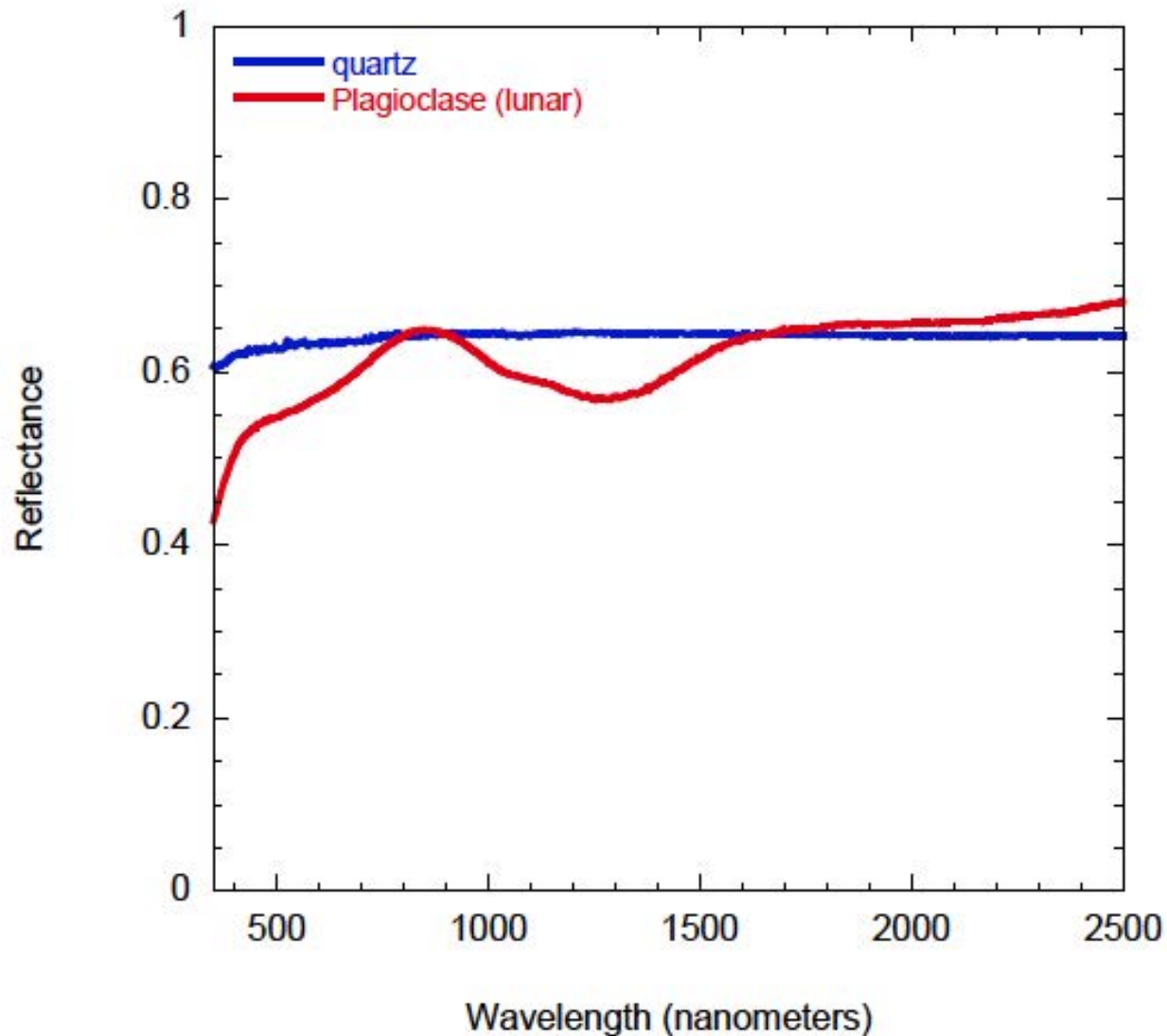


Spectra can indicate pyroxene composition



Klima et al. (2011)

(mostly) Non-Fe-bearing silicate minerals (igneous rock)



Electronic Processes

Charge-Transfer Absorptions

Absorption bands can also be caused by charge transfers, or inter-element transitions where the absorption of a photon causes an electron to move between ions. The transition can also occur between the same metal in different valence states, such as between Fe^{2+} and Fe^{3+} . Absorptions are typically strong. A common example is Fe-O band in the uv, causing iron oxides to be red.

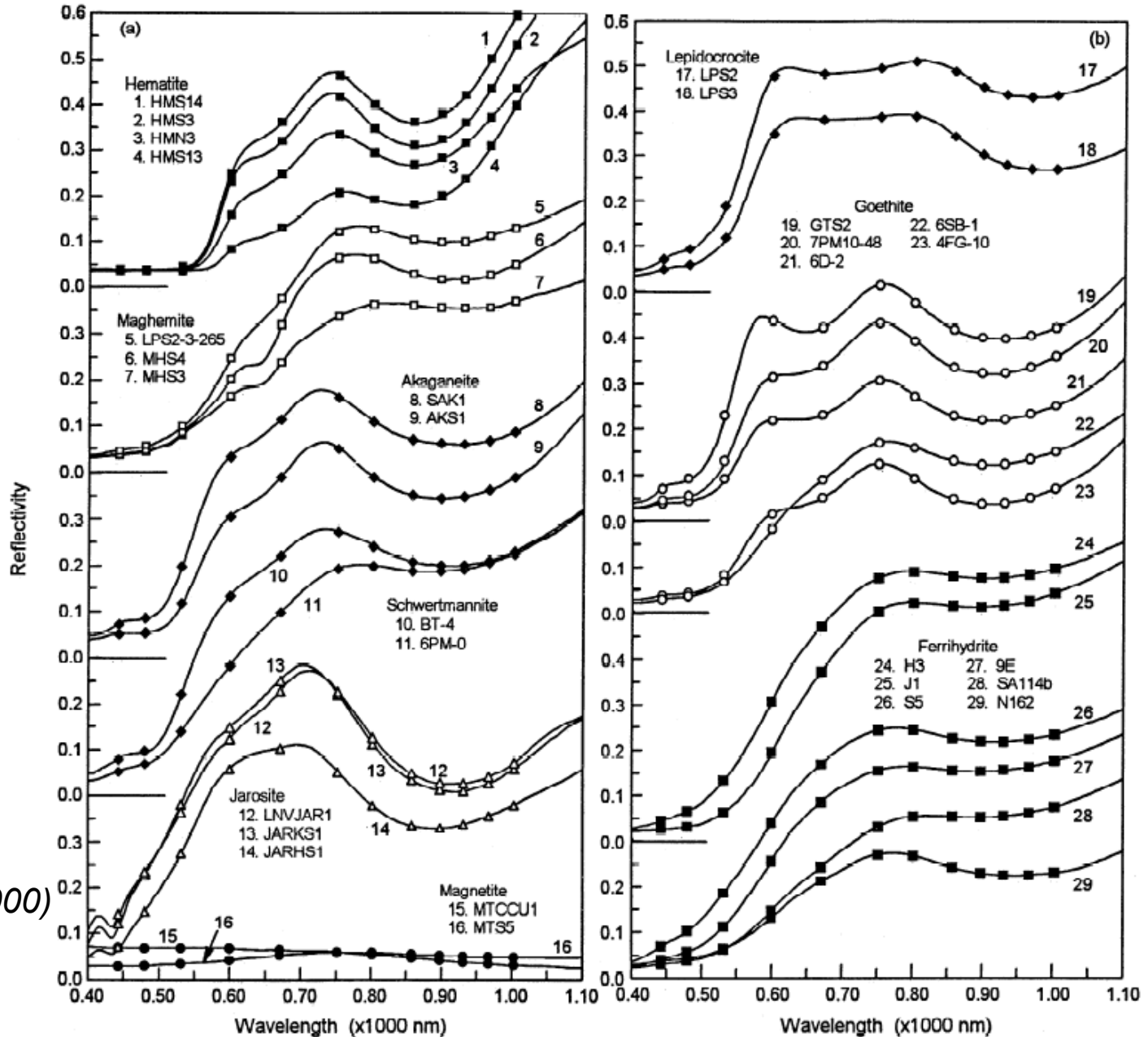


<http://en.wikipedia.org/wiki/Image:Hematite.jpg>



<http://www.galleries.com/minerals/silicate/olivine/olivine.jpg>

Electron charge transfer: why Mars is red!



Morris et al. (2000)

Electronic Processes

Conduction Bands

In metals and some minerals, there are two energy levels in which electrons may reside: a higher level called the "conduction band," where electrons move freely throughout the lattice, and a lower energy region called the "valence band," where electrons are attached to individual atoms. The yellow color of gold and sulfur is caused by conduction-band absorption.

Gold



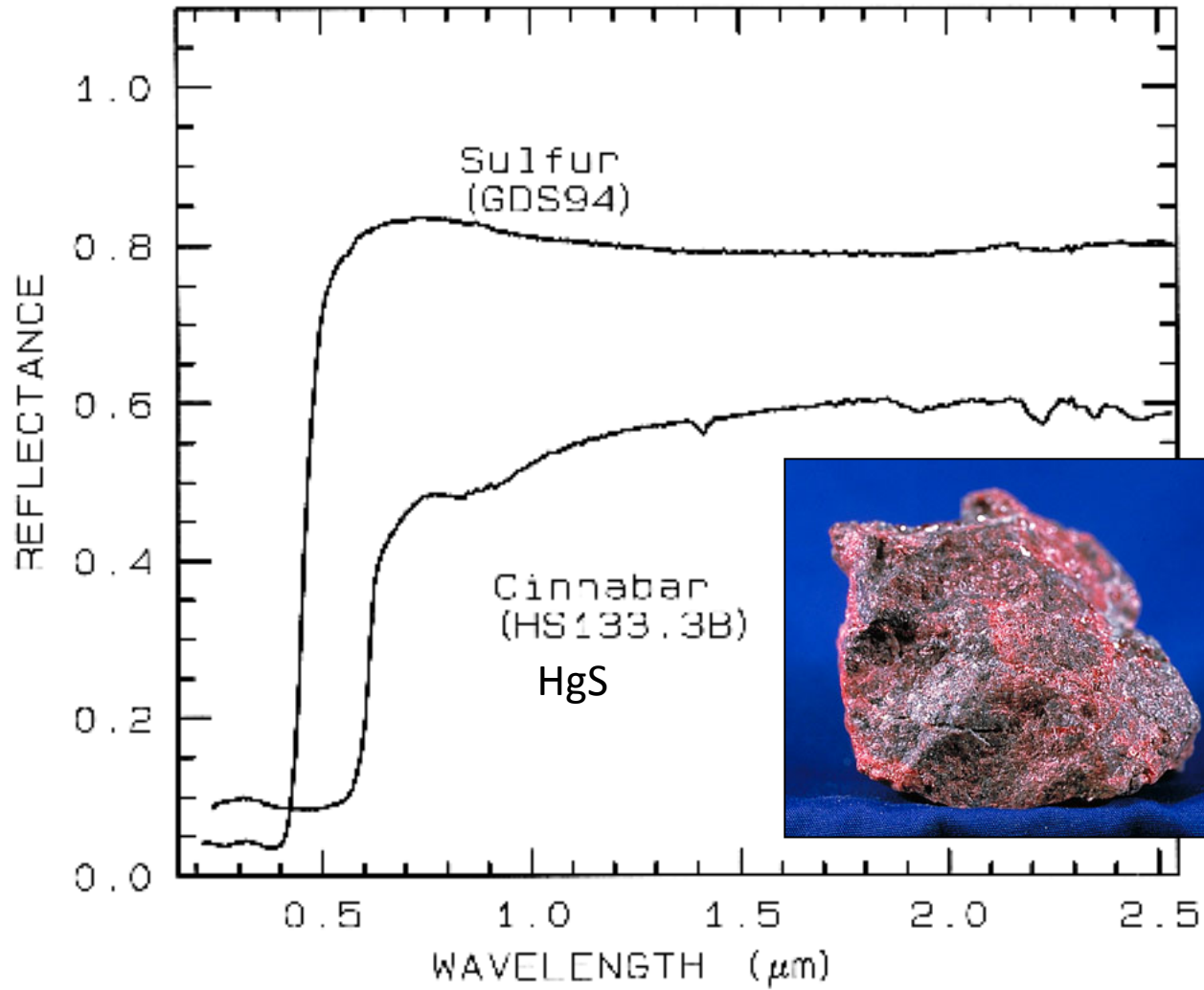
www.egyptcollections.com

Sulfur



web.syr.edu/~iotz/Gallery.htm

Conduction band processes

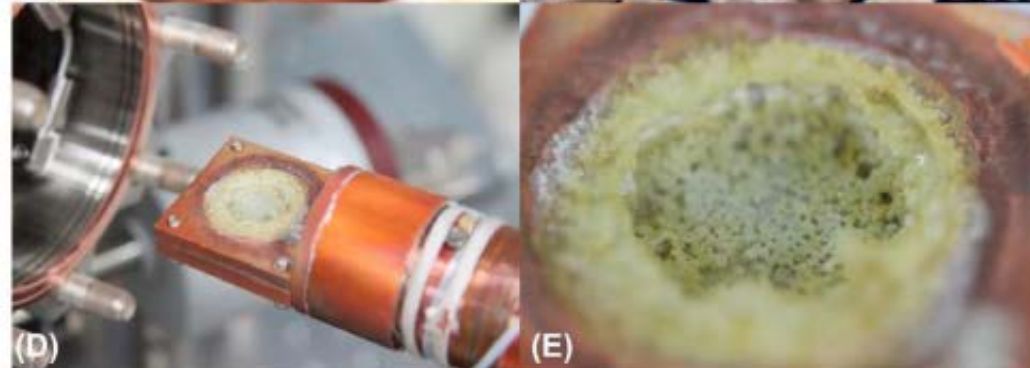
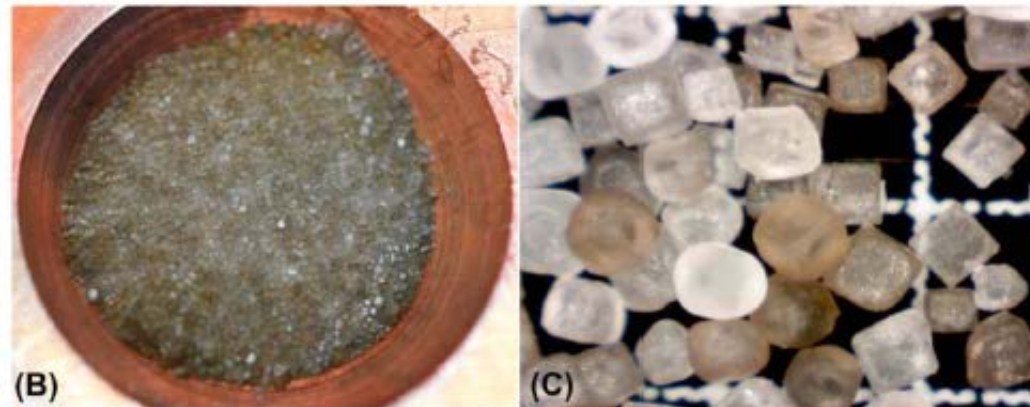
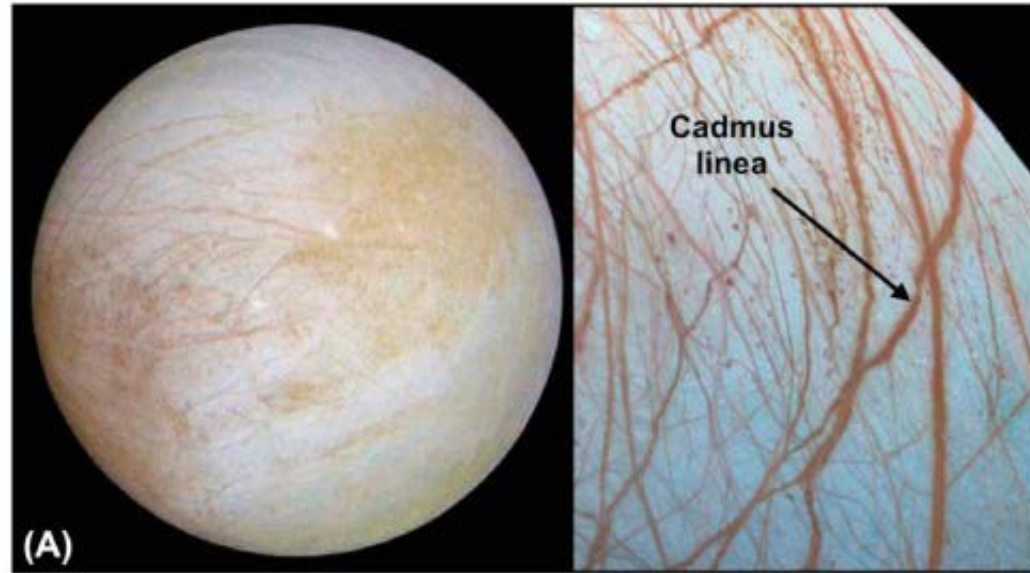


Electronic Processes

Color Centers

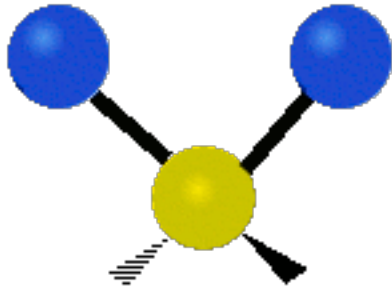
Crystal defects (e.g., induced by radiation) can lead to absorption by materials whose chemical formula otherwise would not suggest any visible/near-infrared features.

At right, NaCl irradiated under Europa-like conditions (Hand & Carlson, 2015)

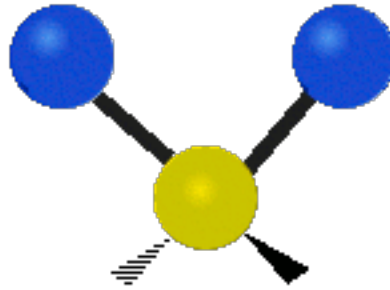


Molecular vibrations

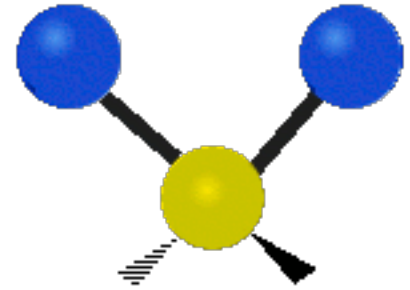
Symmetric stretch



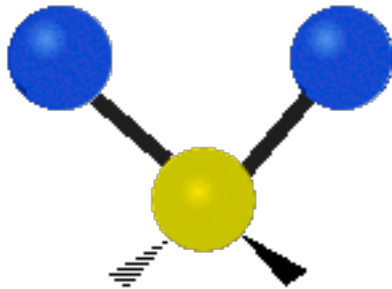
Asymmetric stretch



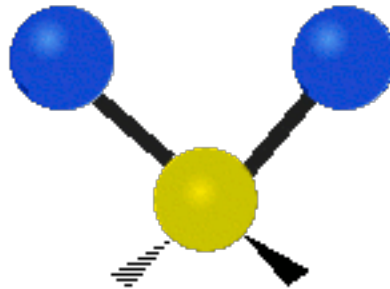
Scissor/bend



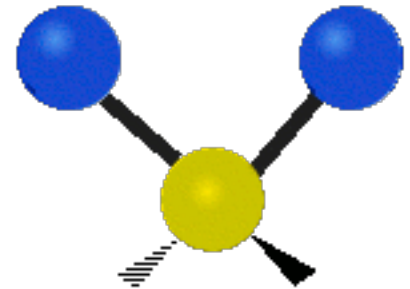
Rocking



Wagging



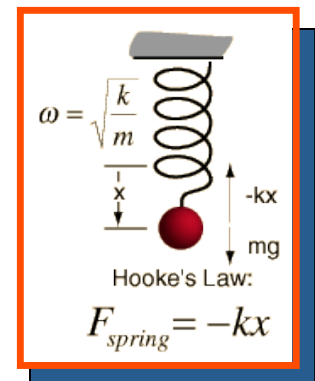
Twist

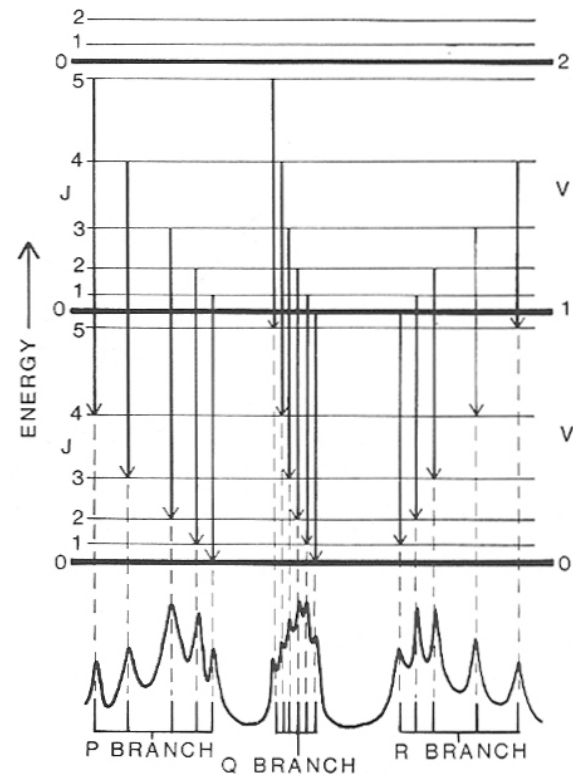
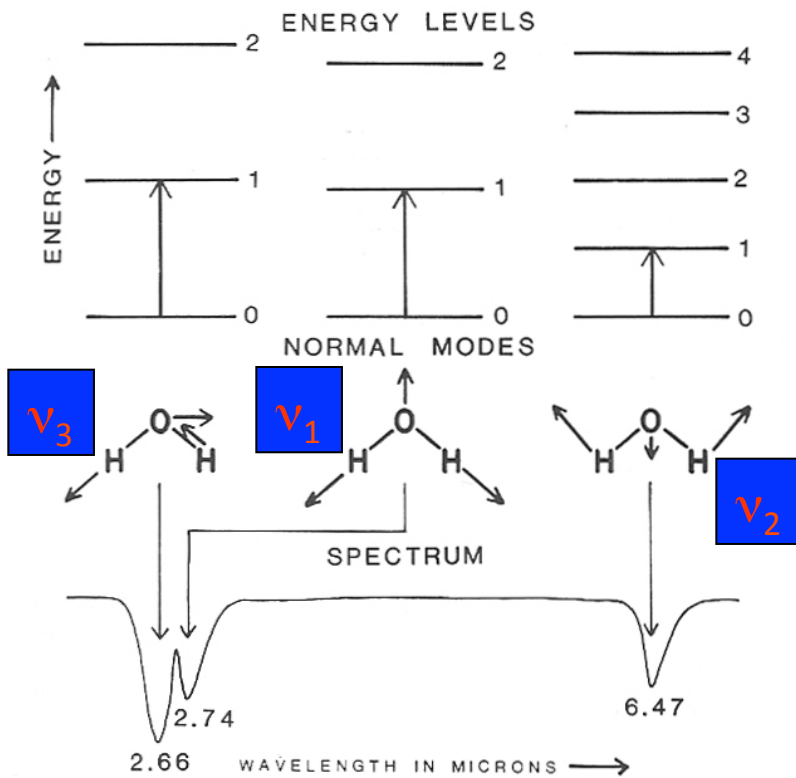


Vibrational Processes

The bonds in a molecule or crystal lattice are like springs with attached weights: the whole system can vibrate. The frequency of vibration depends on the strength of each spring (the bond in a molecule) and their masses (the mass of each element in a molecule). For a molecule with N atoms, there are $3N-6$ normal modes of vibrations called fundamentals.* Each vibration can also occur at multiples of the original fundamental frequency (overtones) or involve different modes of vibrations (combinations).

* In general, a molecule with N atoms has $3N-6$ normal modes of vibration but *linear* molecules have only $3N-5$ normal modes of vibration as rotation about its molecular axis cannot be observed.





Vibrational modes
produce simple spectra

Vibrational - rotational modes
combine to produce complex
spectra with sharp bands

Vibration in water molecules

Water vibrations: ice vs. hydrated minerals

A – D are Europa,
E is Ganymede,
F is model ice spectrum

