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LIGHT WITHOUT HEAT
LUMINESCENCE IN MOONLIGHT, VIDEO SCREENS AND OTHER STORIES

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History

On the night of April 18–19 1787, the famous English astronomer William Herschel was observing the Moon in the vicinity of the crater Aristarchus. He observed a transient luminous phenomenon consisting of spots which he described as glowing like slowly burning charcoal thinly covered with ashes. Herschel did not understand what he was seeing and attributed the phenomenon to volcanoes on the Moon.

The year of 1787 was an unusually active year for the Sun. That is, the number of sunspots that could be seen on the sun was the greatest for several years. The number peaked in about May of 1787. In fact, around the time Herschel was observing his glowing spots, the *aurora borealis* was visible as far south as Padua in Italy. This is rare and is only possible during years of exceptional solar activity.

What was Herschel really seeing on the Moon? How was it related to the aurora and the solar activity? What does it have in common with your TV video display tube? This lecture aims to explore the connections between these things.

The solar activity indicated by the number of Sun-spots as a function of time. *Modified from Abell Morrison and Wolf.*

Luminescence

Herschel's observations of the Moon, the aurora light and a TV video tube all display the phenomenon of luminescence. Before commencing a discussion of luminescence, a few definitions are necessary. The term luminescence can be applied to any object that emits light in addition to the usual reflected light. The main characteristic of luminescence is that the emitted light is an attribute of the object itself, and the light emission is stimulated by some internal or external process. This process is quite different to the *incandescence* seen in an ordinary light bulb filament. In this case the energy from a current of electricity is transferred directly to the metal atoms of the wire. This causes them to vibrate and hence heat up. The wire can then glow white hot, as in an incandescent light bulb. A characteristic of this type of light is that it is accompanied with a great deal of heat! The electrical energy is converted into radiation with an efficiency of about 80%, but the visible light being emitted is less than 10% of the total radiation. The remaining radiation is mainly in the form of infra-red heat. The spectrum of radiation emitted from a hot wire, or any other object, is not sensitive to the attributes of the object. All hot objects emit light and heat with very similar characteristics and this is well described by models based on a generic *blackbody*.

The radiation spectrum emitted by a hot blackbody, such as the filament of an incandescent light bulb operating at several temperatures. Notice how only a narrow band of the radiation is visible to the eye.

Fluorescence

Several types of luminescence can be recognised. Some objects, when illuminated by light of one colour, are stimulated to emit light of another colour. This is called *fluorescence*. A common example is the chemical residue left behind in clothes by some types of washing powders. These powders emit visible light when stimulated by invisible ultra-violet (UV) light found in sunlight. Thus the clothes containing the residues appear brighter because of the combined effect of the reflected visible sunlight and the fluorescence from the washing powder residues. Another example is the chemicals that coat the inside of fluorescent tubes. In these tubes the UV light comes from excited mercury vapour inside the tube. The energetic UV light excites electrons in the fluorescent chemicals which then emit visible light (with a small amount of heat) upon decaying back to their original states. The term *photoluminescence* is sometimes also applied to this type of luminescence which is stimulated by light of another colour.

Another example of fluorescence is in the modern machines for producing medical x-ray images. A screen that produces a lot of visible light fluorescence when irradiated with x-rays is used to form an image which can then be photographed with film sensitive to visible light. This process is more sensitive than using the film to record the x-rays directly, thus minimising the dose of x–rays to the patient.

Phosphorescence

In some materials, electrons excited by the original radiation can take some time to decay back to their ground states. The decays can take as long as hours or days. This type of fluorescence is called *phosphorescence* and the material continues to emit visible light for a while after the original radiation has been switched off. If the duration is very short, around 10^{-7} s, then the material is a *short persistence phosphor*. If it lasts for seconds or longer it is a *long persistence phosphor*. Objects displaying phosphorescence are sometimes said to be *luminous*. Most luminous toys, stickers and watch dials are coated with long persistence phosphors.

Electroluminescence

Another type of luminescence is that produced by some crystals when an electric current passes through them. In this case the current of electrons excites electrons that occupy energy levels involved with chemical bonds inside the crystal. When the excited electrons decay back to their ground states they emit visible light. This is known as *electroluminescence*. There are several different methods of exciting electroluminescence from a crystal. In one method, AC voltages applied to special panels produces light. About 40 years ago, it was thought this sort of light would replace ordinary light bulbs for many domestic applications. This was because electroluminescent coatings could be applied to walls, ceilings, even curtains! There was also virtually no limit to the range of colours that could be produced. Unfortunately, several practical difficulties could not be overcome, such as efficiency, and that high frequency AC was required to excite the luminescence. However, the light emitting diode (LED), operating on a different principle, has now become a widely used application of electroluminescence. LEDs are discussed further later.

Chemoluminescence

In some chemical reactions, energy can be transferred to electrons in the chemical bonds. As these electrons decay down to lower excited states, they emit light. Some of these reactions proceed slowly, so the light can be emitted for a considerable time. This is known as *chemoluminescence*. This is distinct from more vigorous chemical reactions where so much heat is released that the chemicals actually catch fire or otherwise glow red hot. This is nothing more than incandescence. Chemoluminescence is displayed by a variety of organisms and the chemical reaction usually involves the oxidation of a special light producing chemical called luciferin. This is an organic molecule with two hydrogen atoms attached, symbol LH_2. With the aid of the molecule responsible for the storage of energy in cells, adenosine triphosphate (ATP) and a special catalyst molecule (the enzyme luciferase), the luciferin is oxidized to L=O in an excited state. When it changes into the ground state a visible light photon is emitted. One visible light photon alone is emitted as each molecule of luciferin is oxidised, so this really is light without heat. The light is typically light blue in colour, although differing chemical environments can modify the colour. It is believed that this light producing process evolved as a small side branch of the main oxidation-reduction reactions that extract energy from nutrients. Some synthetic molecules, such as Luminol (5-aminophthalhydrazide) and Cyalume are the basis of commercially available chemoluminescent products. Remarkably, some of the steps that lead to the production of light from these chemicals remain to be fully understood.

Cathodoluminescence

Fluorescence, phosphorescence, electroluminescence and chemoluminescence are all very interesting, but they will not help us to understand the observations of Herschel of the Lunar luminescence. For this, it is necessary to introduce two additional forms of luminescence. As long ago as the middle of the last century, it was observed that invisible *cathode rays*, produced by electrical discharges in evacuated tubes, produced light when they struck the glass walls of the tube. The modern name for cathode rays is *electrons* and this type of luminescence is has retained the name *cathodoluminescence*.

This is a very useful form of luminescence. Beams of electrons are used for may purposes. The electron microscope employs beams of electrons to produce high resolution images of small specimens. In some cases, the beam produces cathodoluminescence from the specimen. This is particularly useful for the study of minerals in rocks where the presence of transition metal trace elements can cause the mineral to give of a distinctive colour light. Often the presence of the trace element cannot be detected in any other way. Also, the ubiquitous video display tube also employs beams of electrons to selectively excite red, green or blue phosphors to display colour images. This is such an efficient process that despite continuing revolutions in the semiconductor industry, the video display industry remains dominated by the nineteenth century technology of the video tube.

Ionoluminescence

A more exotic method of producing luminescence is the light produced when fast ions collide with matter. This is called *ionoluminescence*. As yet, this has not been investigated very much in the laboratory, although a research project is now underway here in Melbourne. As we shall see, ionoluminescence is essential to explain the observations of Herschel on the Moon.

An early application of ionoluminescence was to luminous clock dials. These relied upon a rather hazardous method of making light that involved radioactivity. A radioactive material, such as radium, was mixed with a material that displays luminescence, such as zinc sulphide. As the radium decays, it emits alpha particles and other radiation. This excites electrons in the luminescent material to give off light. This is very handy, since the light persists indefinitely, limited only by the half-life of the radium isotope used, ^{226}Ra, which is 1600 years! However, such clock dials are dangerously radioactive. In fact in the late nineteen twenties, several workers at a luminous dial painting factory were severely injured or killed from ingesting radioactive material as a result of licking their paint brushes to get a fine brush point.

The Mechanism of Luminescence

The most important characteristic of luminescence is that it is an attribute of the material producing the light, and not the method used to excite it. The production of luminescence from a solid material can be understood from the *band theory for solids*. This is a theory based on elementary atomic physics and quantum mechanics. The theory is briefly introduced here.

An isolated atom carries its collection of electrons in electron orbitals surrounding the nucleus. These orbitals are analogous to the orbits of the planets around the Sun, although in that case gravity binds the system instead of the electromagnetic force as in an atom. The electrons can only occupy special orbits that allow them to orbit without loosing energy. These allowed orbits may be determined from the laws of quantum mechanics. Also, owing to the fact that electrons can share their orbitals with at most one other electron of the opposite spin (the *Pauli exclusion principle*), some electrons must occupy orbitals far from the nucleus because

Energy levels of the hydrogen atom showing the energy of the allowed electron orbitals.

the lower energy orbitals closer to the nucleus are already occupied.

Vacancies can be created in occupied orbitals by dislodging the electron occupant with a pulse of radiation such as from a photon, a fast electron or some other process. When this occurs, an electron from an outer level will fall down to reoccupy the inner, lower energy, level. The excess energy is radiated away as a photon. For some transitions, this photon can be within the visible spectrum. A larger transition produces a higher energy photon which may be in the x–ray region. Gases in discharge tubes that are bombarded by currents of electricity can display a spectrum characteristic of the transitions between the allowed energy levels in the solitary gas atoms.

In a solid, the situation is more complicated. When individual atoms are joined together to make a solid, the atoms must be pushed relatively close together. When this happens, the outer electron orbitals begin to overlap. Since no more than two electrons can occupy the same level, the energy levels begin to split into sub-levels. If six atoms are joined together to make a small lump of material, the orbital of the outermost electron overlaps with the adjacent atoms and splits into six to accommodate all electrons. These new orbitals are associated with the entire lump, rather than just a single atom. If millions of atoms are joined together to make a sizable lump of material, the outer orbitals overlap and split into millions of sub-levels, all with slightly differing energies. In practice, the energy levels are so close together, and there are so many of them, we can speak of the orbital now consisting of an *energy band.*

On a small scale, the solid consists of a crystal with all atoms occupying lattice sites. Some normal solids, of interest here, consist of large assemblages of microscopic crystals. The luminescent properties of the solid depends on the properties of the crystal structure.

The formation of energy bands occurs regardless if the energy levels are occupied by electrons or not. Therefore, in a typical material, the outermost electrons occupy a band called the *valence band*, above which is the next higher energy band called the *conduction band.* The energy difference between the highest energy (top) of the valence band and the lowest energy (bottom) of the conduction band is called the *band gap energy.*

If the valence band is completely full of electrons, the material is an insulator, since to conduct electricity the electrons must pick up energy and move to a slightly higher level. Since all available levels in the valence band are full, they cannot do this, and the material is

The formation of energy bands for the outer orbital electrons when atoms are joined together to make a lump of material.

an *insulator*. Of course a really vigorous shove can displace an electron into the unoccupied conduction band, but the energy required to do this is greater than normally associated with the flow of electric currents.

The energy bands in a typical solid. The nuclei of the atoms of this solid are shown by + signs. Orbitals close to the nuclei are essentially unaffected by the formation of the solid, so transitions between the lower levels can produce x–rays characteristic of the original atoms. This is not the case for transitions between the outer (higher energy) orbitals forming the bands, such as between the conduction and valence bands shown here. The interatomic spacing is typically 0.5 nm (1 nm = 10^{-9}m). *From Yacobi and Holt.*

If the valence band is only partially occupied, then the material is an electrical *conductor* since there are free energy levels available for the electrons to carry the electric current. Owing to the fact that the valence band is formed from the outermost occupied orbitals of the atoms, which can contain either one electron or two electrons of opposite spins, the valence band in any material is always either entirely full (insulators), or just half full (conductors).

In some materials, the gap between the fully occupied valence band and the empty conduction band is very narrow. So narrow in fact that ordinary heat energy at room temperature can promote electrons from the valence band into the conduction band. Such materials are *semiconductors*. These are generally poor conductors compared to metals.

The band structure of insulators, conductors and semiconductors.

When any solid material is excited by energetic radiation, electrons can be excited out of the valence band into the conduction band. This leaves behind a hole in the valence band. The electron in the conduction band can dissipate excess energy as small amounts of heat until it reaches the lowest energy (bottom) edge of the conduction band. It can then fall back into the hole in the valence band, radiating the energy difference as a photon.

Doping

As can be seen from the table of band gap energies, few materials have band gaps where the width corresponds to the visible spectrum. However, materials with a relatively wide band gap can be made to luminesce in the visible. This is possible by the addition of different atoms or imperfections into the crystal. The additional atoms, called *dopants* have a different electron orbital structure compared to the host crystal lattice. Therefore, in regions of the crystal around the dopant atom, additional energy levels become available. That is, within the forbidden band gap of the material, energy levels can exist than can accommodate electrons or holes. These levels can be close to the conduction band, in which case the dopant is called a *donor*, or close to the valence band, in which case it is called an *acceptor*. Transitions between these levels can give rise to visible luminescence in which case the dopant is known as an *activator*. In most cases, the activator is present in extremely small concentrations, ranging from as much as 1 dopant atom in 5000 host atoms down to as little as 1 dopant atom in 5 billion host atoms!

Chemical formula of solid		Band gap energy E_g (300K) eV	Band gap wavelength λ_g (nm)	Colour
C (diamond)	I	5.47	230	UV
ZnS (ZB)	D	3.68	340	UV
ZnO	D	3.35	370	UV
ZnSe	D	2.58	480	Blue
CdS	D	2.42	510	Blue/Green
ZnTe	D	2.28	540	Green
GaP	I	2.26	550	Green
SiC (ZB)	I	2.20	560	Green
AlAs	I	2.16	570	Green/Yellow
CdSe	D	1.74	710	Red
AlSb	I	1.58	780	IR
CdTe	D	1.50	830	IR
GaAs	D	1.42	870	IR
InP	D	1.35	920	IR
Si	I	1.12	1060	IR
Ge	I	0.66	1900	IR
PbS	I	0.41	3000	IR
Sn	D	0 (metal)	–	–

Band gap energies, E_g, and associated band gap transition wavelengths, λ_g, for some semiconductors. D indicates that a transition directly across the band gap can conserve momentum and is therefore possible. I indicates that a direct transition is not possible and a lattice vibration, or phonon, is necessary to conserve momentum and so only indirect transitions are possible. ZB indicates the zinc blende form of the crystal.

The phosphors in vacuum tube video display tubes rely on phosphors formed from activators. For example, ZnS doped with silver (Ag) or chlorine (Cl) produces blue light, ZnS doped with copper (Cu) or aluminium (Al) produces green light and Y_sO_2S doped with europium (Eu) produces red light. Transition metals like Ag and Cu have partially-filled 3d outer shells which make transitions highly sensitive to the surrounding crystal field. The resulting luminescence spectrum is a broad, featureless shape, as can be seen spectrum in the figure for a green phosphor. On the other hand, rare earth metals like Eu have an unfilled 4f shell which is shielded from the surrounding crystal field by a filled 5s,p,d outer shell. Consequently the transitions which occur at rare earth metal impurities are sharp. This can be seen in the spectrum in the figure for a red phosphor.

Sometimes the excited electron can find other ways to dissipate its energy. Several *non-radiative* recombination mechanisms are possible. These are usually associated with defects in the crystal, or levels in the middle of the band gap, called *deep levels*, introduced by impurities called *inhibitors*. Still other defects in the crystal can result in *shallow levels* which are close to the edge of either the valence or conduction bands. Shallow levels in the band gap can trap the excited electrons. Certain characteristics of these shallow level prevent the electron from decaying immediately back into the valence band. Instead the decay may only occur spontaneously after a very long time. However a small amount of heat may dislodge the electron back into the conduction band from where it can readily decay back to the valence band. This is the mechanism behind the technique of *thermoluminescence*. Some materials can be dated by measuring how much light they produce when heated. This measures the remaining electrons trapped in the shallow levels and hence how long is has been since the original excitation promoted the electrons.

Ionoluminescence of TV tube phosphors for (left) green and (right) red. *Data from the Melbourne nuclear microprobe.*

Filling and emptying of shallow level traps in the band gap to produce luminescence. *From Sproull.*

Semiconductor devices

Semiconductor devices utilise other methods of stimulating light from the band gap. Most elemental semiconductors come from column four of the periodic table, for example silicon and germanium. Elements in this column have four valence electrons and can form crystals in which each atom is symmetrically bonded with four neighbours. If an atom from column three (e.g. aluminium or gallium) is added to the lattice it acts as an acceptor. This atom has one less valence electron available for bonding. However it can temporarily borrow the 'missing' electron from somewhere else in the lattice. This creates a positively charged *hole* in the crystal lattice since the associated column four element is now missing one of its outer shell electrons. Acceptor levels also appear in the band gap. Because of the positively charged holes in the lattice, which can carry electric current, the material now conducts electricity better than before and is called a *p–type* semiconductor.

Similarly, an element from column five (e.g. phosphorus or arsenic) acts as a donor. When added to a semiconductor crystal it has an extra bonding electron that can drift away from the donor element. Donor levels appear in the band gap. A region of net negative charge is created in the vicinity of the drifting electron which can carry electric current. Once again, the material conducts electricity better than before and is called a *n–type* semiconductor.

Two dimensional representation of a semiconductor crystal containing (*left*) a donor atom or (*right*) an acceptor atom. *From Serway et al.*

In a diode, a slab of p–type material is joined to a slab of n–type material. The free holes and electrons can combine in the vicinity of the junction. This creates a region depleted of these charge carriers called a *depletion region.* Because of the combination, the n–type material next to the junction becomes positively charged and the adjacent p–type material becomes negatively charged. Electric currents can only pass through the junction if the electrons in a circuit are injected in to the n–type material. The electrons pass through the n–type material and combine with a hole at the junction. An electron can then leave the p–type material to complete the circuit, creating a new hole. Thus the electric current is effectively carried by holes in the p–type material. The diode is *forward biased.*

If electrons are injected into the p–type material, the charge carriers are holes, not electrons. There is no mechanism to transfer the electron through the p–type material and across the junction. The diode is *reversed biased* and no current flows. In fact the depletion region grows wider.

Normally, in a forward biased diode, free electrons do not continue across the junction into the p–type material. However, under conditions of extreme forward bias, electrons can be injected across the junction into the p–type material and holes can be injected, in the reverse direction, across the junction into the n–type material. When this happens, the surplus electrons recombine with holes in the p–type material and the holes with electrons in the n–type material. That is, transitions occur across the band gap and light is produced. This is a *light emitting diode* or LED for short.

Modern semiconductor device fabrication techniques allow *band gap engineering* and junctions can be produced from special materials in which the band gap energy corresponds to almost any wavelength in the visible light spectrum. Such materials usually consist of compounds of (left) The internal electric field and resulting potential from the combination that occurs in a p–n junction in a diode. (right) A forward biased diode and the resulting light emission. *From Serway et al.*

equal amounts of elements from columns three and five (e.g. GaAs) or columns two and six (e.g. CdTe). Notice how the average four bond structure is maintained! As a result of this, LED's are now available in all colours of the rainbow allowing the possibility of semiconductor displays in which each pixel is a tiny array of one red, one green and one blue LED. Each LED is individually controlled by video circuitry to produce the correct combination of colours for the picture being displayed.

The spectra of commercially available visible light LEDs.

Still other semiconductor devices utilise another method to produce light. When electrons are confined to small places, they can no longer move about freely. If the confinement is tight enough, the electrons begin to display their quantum mechanical characteristics associated with their wave–like attributes. They can only occupy discrete energy levels in their confinement. Transitions between these allowed energy levels can radiate visible light. Such devices are called *quantum wells*. These devices represent the cutting edge of semiconductor device technology.

Conclusion

So at last it is possible to understand Herschel's observations of luminescence from the Moon and its connection with the Sun's activity. During periods of intense activity on the Sun, large numbers of energetic protons are produced that stream out from the Sun as the solar wind. Without a shielding atmosphere, these rain down on the surface of the Moon and induce luminescence from the minerals on the surface. Clearly, the minerals in the vicinity of the Aristarchus crater must contain crystals with transitions in the band gap corresponding to red light. This is also commonly seen in terrestrial minerals, or in the red phosphors of a TV tube! Thus Herschel was observing ionoluminescence of the Moon.

The intense streams of protons also interacted with the Earth's atmosphere. Fortunately for life on Earth, the atmosphere shielded the surface of the Earth from the protons. But the energy deposited by the protons in the rarefied gases of the outer atmosphere induced fluorescence, causing the unusually bright aurora visible in Italy at the same time as Herschel's observations.

Modern observations of the lunar luminescence phenomenon reveal that the ionoluminescence is strongly present after solar flares, when an extra flood of protons is given off by the Sun. It is also possible to observe the lunar luminescence during an eclipse of the Moon by the Earth. In this case the Moon is shielded from direct sunlight. The positively charged protons can bend around the Earth in magnetic fields and still strike the Moon.

In 1787, at the time of Herschel's observations, the electron had not been discovered and the theory of the atomic structure of matter had not been developed. It was not surprising that Herschel misapprehended the origin of the lunar luminescence. I think he would have been astounded to learn that in the late twentieth century, many people spend a good part of their lives gazing at essentially the same phenomenon produced by the video tubes of their television sets!

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DEMONSTRATIONS

- Light bulb connected to a variac to show stages of heating.
- Spectrum from a blackbody showing IR/VIS/UV components.
- Fluorescence of washing powder and other objects when excited by UV light.
- Fluorescent tubes showing various coatings.
- Spectrum from fluorescent tubes showing spectral lines – contrast with incandescent light bulb.
- Phosphorescence of fluorescent tubes after switching off.
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- Energy levels around an atom.
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