

Sharon Elaine Thompson

Painting the Ruby Red

First published in *Lapidary Journal*, March 1992

Our world would be a much duller place without the property of color, a magic trick of the phenomena of light.

If rocks and minerals came in shades of black and white and gray, the chances are good there would be no Tucson Gem and Mineral Show. There would be few minerals we would consider gems. Oh, we might value certain minerals such as quartz, tourmaline, corundum, for their industrial properties. But in a world where color is often a criteria for beauty--whether it is in the leaves of fall, the fashions of spring, or a friend's eyes--we would almost certainly not treasure rocks and minerals for their beauty. For without color a gemstone (with the notable exception of diamond) is just another rock.

When you think about it, the rainbow of reds, greens, yellows, blues, and purples on which we feast our eyes at Tucson is nothing short of a miracle. Forget the odds against a gem-quality crystal forming in the first place. Forget the odds against it surviving to reach the surface. And forget the odds against someone discovering it, cutting it, and bringing it to Arizona. The fact that it has color at all is amazing enough.

For nature to paint the ruby red, the right atoms of the right elements must be in the right places in the right amounts. And then these minute bits of matter must all be coordinated with the mercurial nature of light. For without light, gemstones, no matter how perfect their atomic recipe, would have no color.

Light is a kind of electromagnetic radiation, part of the continuous spectrum of energy given off by the sun. The electromagnetic spectrum includes everything from very high energy, very short wavelength cosmic, gamma, and x-rays, through short microwave and ultraviolet wavelengths, down to very low energy, very long wavelength infrared and radio waves. But most of the energy our star produces is in the visible light range, sandwiched in between ultraviolet and infrared. (The California Institute of Technology's eccentric physicist, Richard Feynman, used to call all forms of electromagnetic energy "light." Most commonly, though, the word "light" is used only for energy wavelengths we can see or *visible light*.)

Light falling from the sun seems to have no color. We call it "white" light. But as Sir Isaac Newton showed in the early 1700s, white light is just chock full of color. Newton passed a beam of sunlight through a prism separating it into the familiar colors of the spectrum: red, orange, yellow, green, blue, and violet. This was not remarkable in itself. Newton was not the first to be fascinated with the colors produced by a prism. But he was the first to realize that the resulting colors were not generated by the glass prism, but were part of the light itself.

Each color of the visible spectrum corresponds to a range of energy, although the ranges overlap. Because light is dual in nature, sometimes behaving like a particle and sometimes like a wave, we can describe colors both ways.

In gemology, we commonly describe colors in terms of wavelength. (A wavelength is the distance measured from the crest of one wave of light to the crest of the next.) The short (close together) violet wavelengths of light have the highest energy in the visible light range; the longer (farther apart) red wavelengths have the lowest energy. Wavelengths in the violet end of the spectrum are about 400 nm long; wavelengths in the

red end of the spectrum are about 700 nm long. (Nm is the abbreviation for nanometer, the unit of measure often used for electromagnetic wavelengths. A nanometer is one billionth of a meter.)

But we can also think of a color as a bunch of *photons*, particles of light, containing similar amounts of energy. (Newton described light particles as having different sizes, and that helps to visualize things a bit.) You might have photons with energy levels that correspond to wavelengths of 700 nm, 698 nm and 692 nm but they would all contribute to the color red.

Color in gemstones is generated when the photons in light interact with the billions of atoms that make up a gemstone. In gemstones, the color-causing atoms that respond to the stimulation of light energy are often ions of metallic elements, such as chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), titanium (Ti), and vanadium (V), which are dispersed, or spread, throughout the material. These ions can be present as impurities in a mineral (called *allochromatic* gemstones), or they may be an intrinsic part of the minerals chemical composition (*idiochromatic* gemstones).

As photons of light penetrate a gemstone, they may run into atoms, in particular the electrons in the atom. If conditions are right, the electron absorbs the photon. This boost in energy shoves the electron to a higher energy level. An electron that is temporarily in a higher energy level is said to be in an *excited state*.

Metal ions are more excitable, to use an incorrect term, than other atoms. In more stable atoms, the electrons are paired up. Photons of light have difficulty dislodging them. But the electrons in metal element ions are unpaired. They are more susceptible to stimulation by light energy and so are more likely to jump to an excited state.

This is important to the creation of color in a gemstone because in the process of absorbing energy, the electron also absorbs the color that corresponds to that energy wavelength. In effect, that color disappears from the light. The unabsorbed wavelengths of light are reflected or transmitted by the gemstone. It is these leftover wavelengths that reach our eye and cause the color we see in the gem.

For example, a ruby absorbs yellow and green wavelengths of light and usually much of the blue. Only red wavelengths are transmitted or reflected to the eye. Because these wavelengths are the only ones we see, rubies appear red. If blue is also transmitted, the ruby becomes purplish.

The electron excited by light does not stay in its excited state permanently. It almost immediately falls back to its original energy level, or its *ground state*. It is a law of physics that energy can be neither lost nor destroyed. So as the electron returns to its ground state, it releases the same amount of energy it absorbed from the light photon in the first place. However, the energy is usually released as lower level energy of longer wavelength.

Most of this energy is in the form of infrared energy, or heat. But occasionally some of the longer wavelengths released may still be in the visible light range. For example, when rubies emit heat they also emit red wavelengths that intensify the color of the stone.

Gemstones can also absorb wavelengths of energy outside the visible light region. It is not uncommon for minerals to absorb ultraviolet radiation. When the electrons in these materials return to their ground state, they may emit visible light. This is the phenomena we call *fluorescence*.

It would be very nice if we could say that the red in a gemstone was always caused by a chromium ion, or the green in a stone was always caused by iron. However, with the capriciousness of any woman worth her salt, Mother Nature has made sure that nothing is that simple.

The presence of a metallic element ion such as iron (Fe), chromium (Cr), or manganese (Mn), does not guarantee a gemstone will have color. Nor does it necessarily foretell what color a gem will be. The same element may cause different colors in different minerals. Chromium in corundum produces a ruby, but when in beryl it gives us emerald. Even when the same element is the color-causing agent in the same mineral, we may see different colors. Iron in beryl, for example, may create the blue in aquamarine or the yellow in golden beryl.

One factor that can cause differences in color or in intensity of color is a difference in *valence state*. The valence of an atom tells us whether an ion has a positive or a negative charge, and how great that charge is. One element can produce ions of several different valences. Iron, for example, may have two more protons than electrons (Fe^{2+}) or three more (Fe^{3+}), or even four more (Fe^{4+}). In beryl, Fe^{3+} gives us green beryl; Fe^{2+} turns beryl into blue aquamarine. Fe^{4+} turns quartz into amethyst. Mn^{2+} turns beryl pink, but Mn^{3+} turns it red.

Because some valence states produce better--or at least more marketable--colors than others, it stands to reason that some enterprising merchandiser would try to come up with a way to alter a gem's valence state. And in fact, that is what some forms of treatment, such as heating and irradiation, do. They encourage electrons to move in or move out, changing the ion's valence. A change in valence state occurs, for example, when greenish aquamarine is heated to drive off the green and turn the color to blue.

Internal pressures can cause an ion to trigger a difference in color, too. Atoms in a mineral are locked in what could be described as a perpetual love-hate relationship. The electrons, with their negative charge, constantly repel each other, yet they are attracted by the positive charge of their neighbors' protons. These forces, called atomic bonds, are what hold a mineral together in its characteristic way.

The attractive/repulsive forces between atoms are not equal for all kinds of atoms. Some atoms attract each other more, some are more strongly repelled. The strength of the pushing and pulling depends on what kinds of atoms are involved and how they are arranged with respect to each other.

Certain atoms bond more closely. As a result, there is terrific repulsion between their electrons. It's like pushing the negative ends of two magnets together--the closer they get, the more they resist. In these minerals, before an electrons can jump to a higher orbital, they have to absorb a lot of energy from the light. They need more of a "push"--just as the magnets, as they get closer together, need more push to force them even closer. If the atoms in the mineral were farther apart, or less strongly bonded, they would exert less pressure on each other's electrons. It would take less energy, of a lower wavelength of light, to propel the electrons into a higher orbital.

The classic case of this is the difference in color in emeralds and rubies. Both the beryl and the corundum are colored by the interaction of chromium ions with the aluminum (Al) and oxygen (O) in these minerals. However, in the beryl, the presence of beryllium and silicon throws a monkey wrench in the works. The strength of the bonds in one gem is not the same as it is in the other. As a result, the chromium absorbs different wavelengths of light in each of them and we get ruby from one and emerald from the other.

The effect of a difference in atomic bonding strength on color is sometimes quite dramatically (although temporarily) seen by jewelers. Because corundum can usually take a lot of heat, some jewelers do not remove rubies when they retip a prong. (This can be disastrous if the ruby is strained or contains fractures or other inclusions.) As the temperature of the ruby climbs, the bonds between the atoms stretch, and there is not as much repulsion--and the ruby turns green! As the stone cools, the normal color returns.

The forces of repulsion between electrons are sometimes primarily affected by the number of atoms the color-causing ion is bonded to and the arrangement it forms with those atoms. In gemstones, ions can form octahedral, tetrahedral, and distorted cubic groups with neighboring atoms.

In some relationships, the electron orbitals point directly at those of a neighboring atom. The repulsion between the orbitals is intense. It takes a great deal more energy for an electron in the ion to make the jump to a higher energy level.

When the orbitals of the electrons around the ion fall between the orbitals of the neighboring atoms, however, the repulsive forces are less. Less energy is needed to boost an electron to a higher level. Again, because of the different wavelengths of light absorbed, the color of the gemstone may be different. For example, an iron ion in an octahedral grouping is bonded to six atoms; in peridot that produces the mineral's characteristic yellowish green color. But the same ion bonded to eight atoms in a distorted cube makes almandite garnet red.

The changes in energy level that we have examined so far are contained in an ion. The electron moves up to a higher orbital within the atom and then falls back to its ground state. But in some situations, electrons may get so excited by light they take excursions to a completely different atom. Because they pack their negative charge and take it with them, the process is called *charge transfer*.

When the charge transfer process absorbs wavelengths in the visible range of the spectrum, the absorption can be from 100 to 1000 times stronger than the absorption produced by internal ramblings of electrons in dispersed metal ions. As a result, charge transfer between atoms can create much more intense colors.

An itchy-footed electron from the atom next door, which in most gemstones is an oxygen atom, may drop in on a metallic ion. The charge transfer involved in this kind of visit may create yellows, oranges, and browns in beryls and sapphires, or the deep purple of amethyst.

Electrons from an ion, too, may get the urge to wander and go off to visit their kin on the other side of the oxygen atom. For instance, electrons from an Fe^{2+} ion may transfer to an Fe^{3+} ion bonded to the same oxygen atom, and produce the deep blue color seen in some aquamarines. However, charge transfer can take place between dissimilar metal ions, too. For example, ions of iron (Fe^{2+}) and titanium (Ti^{4+}) exchange electrons in corundum to produce blue sapphire.

In some materials, the electrons in the atoms are sort of communal property. They are shared by all the atoms. They are not limited to interactions between individual atoms or small groups of atoms. The levels of energy in the bulk of the electrons are usually so similar that they are called *energy bands*.

Energy bands are most common in the metals. But they can also occur in some gem minerals. In these minerals there are usually two bands: one lower-energy band packed with electrons (called the valence band) and a higher-energy band with virtually no electrons (the conduction band). In between the bands is a region of possible energy levels called the *band gap*. (It's as if you had a room full of balls that you separated into rows of similar sizes. You might have one "band" of soccer balls and one "band" of golf balls. But there would be an area of potential ball sizes in between.) In these materials, electrons jump between the energy bands instead of between the energy levels of a single atom or pair of atoms.

If the gap between energy bands is so small that almost all wavelengths of visible light will boost electrons into the higher band, then all light is absorbed and the material appears black. If the band gap is slightly larger, so that the energy available in visible light

is enough for some electrons to jump the gap, only some wavelengths will be absorbed. These stones are usually yellow, orange, or red.

But if the energy needed to jump the band gap is greater than the maximum energy available in visible light (the violet wavelengths), the electrons cannot make the transition to the higher level. The material will not absorb light; all light striking the stone will be transmitted so the gem appears colorless. This last is the most important group of gem materials colored by this process. It includes colorless beryl, diamond, quartz, and topaz.

Impurities in these stones can create intermediate energy levels between the energy bands. When this happens, there is a much greater likelihood that electrons from the valence band will absorb enough energy to make the jump to this intermediary level or be able to jump from the intermediate level to the conduction band. As a result, light may be absorbed and the gemstone may show color. In diamond, in particular, color can be created this way. When nitrogen impurities are present, they absorb violet to green wavelengths, producing deep yellow "canary" diamonds. Boron atoms in diamond, however, absorb wavelengths in the green through infrared range. The resulting stones are blue.

High energy radiation can cause or cure cancer. It promoted the beginning of life on Earth. And it can create defects in gem materials that cause color. These light-absorbing defects are called *color centers*.

Color centers can occur when irradiation shakes complete atoms out of position, as it does sometimes in diamond. The resulting absorption in the red and orange part of the spectrum may produce blue stones, but it more often produces green diamond.

Most frequently irradiation knocks electrons out of position. This can change the valence state of an ion, for example, converting the Fe^{3+} ion in quartz to Fe^{4+} , and creating an amethyst. Or the process can be more complex. In some quartz, silicon ions may be replaced by aluminum ions. That alone may not cause color. But if the stone is irradiated, either naturally or in the laboratory, the oxygen atom next to the aluminum may give up an electron. The stone will then absorb light throughout the spectrum and turn the quartz dark. The result: smoky quartz.

The alteration in color created by irradiation may be unstable. Heating can often reverse the effect, by relaxing the atomic bonds enough to allow the electrons to go back to their original places. This can happen with laboratory-irradiated diamonds or smoky quartz. Maxixe-type beryl does not even need heat reverse the color. The energy available in sunlight is enough to send the electrons home. The Maxixe will fade on exposure to daylight.

This has been a very simplified overview of the causes of color in gems. But even so, it is obvious that color in gemstones is not as simple as "add 2% chromium and mix well." The awesome and complex design of nature, coupled with chance combine are necessary to make some of the world's most remarkable materials even more amazing.

For more information about the causes of color in gemstones, see "The 13 Colors of Gems and Minerals" by Kurt Nassau, *Lapidary Journal*, February 1988; *The Physics and Chemistry of Color: The Fifteen Causes of Color* by Kurt Nassau; "An Update on Color in Gems," a three-part series by Emmanuel Fritsch and George R. Rossman in *Gems & Gemology*, Fall 1987, Spring 1988, Summer 1988; *The Beauty of Light* by Ben Bova; and *Light* by Richard Morris. My thanks to John Koivula, Senior Staff Gemologist at GIA, Emmanuel Fritsch, Research Scientist at GIA, and George Rossman, professor of mineralogy at the California Institute of Technology for their willingness to answer questions and shed light into some very dark corners.