THE COLORING AND THERMOPHOSPHORESCENCE PRODUCED IN TRANSPARENT MINERALS AND GEMS BY RADIUM RADIATION[1]

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In an earlier paper[2] one of us reported some observations on the coloring, decolorization and thermophosphorescent effects resulting from the radiation of glass by radium rays. Similar experiments, extended to transparent minerals and gems, are described in the present paper.

This subject has already been studied by various investigators.[3] The results recorded here are in the main confirmatory of previous observations, though complete agreement is not to be expected owing to the variations encountered from specimen to specimen of the same material. It therefore seems desirable to report all the results, although many of them duplicate those of previous investigations, in order to be able to consider them together with the other effects described, many of which are new. An additional reason for the joint consideration of decolorization and thermophosphorescence is found in the possible theoretical connection between the two which will be more fully discussed later in the paper.

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[2] S. C. Lind, *Jour. Phys. Chem.*, **24**, 437-43, (1920).

[3] A. Miethe, *Ann. d. Phys.*, **19**, 633, (1906). C. Doelter, "Das Radium und die Farben," Steinkopf, Dresden, 1910, also "Die Farben der Mineralien, Insbesondere der Edelsteine," Vieweg und Sohn, Braunschweig, 1915. E. Newberry and H. Lupton, *Memoirs and Proc. Manchester Lit. and Phil. Soc.*, **62**, No. 10, (1918). St. Meyer and K. Przibram, *Sitzb. Akad. Wiss. Wien*, **123**, IIa, 653-63, (1914). K. Przibram, *ibid.*, **130**, IIa, 265-70, (1921). St. Meyer and E. v. Schweidler, "Radioaktivität," Teubner, Leipsig-Berlin (1916), pp. 191-7; Lit. refs., p. 198. A. Dauvillier, *Comp. rend.*, 171, pp. 627-9, (1920).

The diamond is so unique in its behavior under radium radiation that it will be separately considered in a subsequent communication. In all cases, except the diamond, coloring is produced by the penetrating (beta and gamma) radiation received through a glass wall of ordinary thickness ($\frac{1}{2}$ to 1 mm.). The diamond, however, did not change color under penetrating radiation, even though prolonged and intense, but responded in every case to direct alpha radiation, either from emanation or by direct exposure to radium salts.

Fluorescent effects are caused in some minerals (kunzite, "active" calcite, willemite, etc.) both by alpha and by penetrating radiation, but in most minerals alpha radiation is the only one producing phosphorescence, while many other minerals do not fluoresce even under its stimulus.

In the following, where radiation is reported in terms of *mgs. of Ra*, we refer to the penetrating radiation from high-grade salt (chloride or bromide), 70 to 100 per cent. pure, placed immediately in contact with the mineral and separated only by the glass wall of the container. Where *emanation* is specified, the mineral has been sealed in a glass tube containing radium emanation furnishing alpha, beta and gamma rays. As in the case of glass, the same color is produced in a given specimen (except diamond), either by emanation or by penetrating rays, more rapidly by the former.

Thermophosphorescence was observed visually by placing freshly radiated specimens in an electrically heated muffle, inspecting in the dark with well-rested eye the light emitted upon gradually raising the temperature. In the case of direct radiation by means of emanation the observations were not made until at least four hours had elapsed after removal of the specimens from the emanation in order to allow the active deposit to decay, thus avoiding any direct fluorescent effects.

The observations for individual minerals were as follows:

Rock salt is readily colored to an amber yellow by 250 mgs. Ra in one to two days. It is easily restored to colorless by heating to 300° C. without thermophosphorescence, or by exposure to direct sunlight for one to two hours. Decolorization by diffused light is much slower. The cycle can be indefinitely repeated from color to colorless, either by heat or light, and back to color by radiation.

Through the kindness of Drs. A. W. Hull and W. P. Davey of the General Electric Company, X-ray diffraction spectrographs by the powder method[4] were made both of the colorless and of radium-colored crystals. The two lattice patterns are identical, showing that no change is produced in the colored specimen which can be detected by the X-ray spectrographic method.

Fluorspar.—Different varieties, purple, green, rose, and colorless, are readily colored in one to three days by 250 mgs. Ra to various shades of blue and greenish-blue, which color is easily removed by sunlight or by heat. Thermophosphorescence is striking (next in intensity to kunzite) and like kunzite begins at a low temperature. At 70° C. the light is blue, changing to greenish-blue at 125° and remaining unchanged at 150°. At about 180° the crystals decrepitate and the color produced by radium is discharged. A specimen of rose-colored fluorspar could be colored bluish-green repeatedly under radiation and the rose color repeatedly restored either by heating or by light. On the contrary, the purple variety became white at the decrepitating temperature and could not again be colored by further radiation. These observations appear to support the organic coloring theory for the purple varieties, but not for the rose colored.

Kunzite.—Different specimens of California kunzite behave with remarkable uniformity both as regards coloring and thermophosphorescence. Under radiation from 50 to 100 mgs. Ra, the original lilac color vanishes and the crystal after twenty-four hours' radiation is almost white, which may be due to color compensation by the green color being produced. In two days the green color is well developed and reaches a maximum about the third day, approaching an emerald green, though somewhat lighter. The color is readily restored to lilac, either by light or by heat, and by ultra-violet light in remarkably short time. The cycle can be repeated indefinitely, apparently without fatigue. Fluorescence under penetrating or alpha radiation is of a characteristic orange-yellow or salmon-yellow, and less brilliant phosphorescence has been observed for more than a month after cessation of radiation. In the long duration of phosphorescence it resembles calcite as well as in the color of the phosphorescent

[4] A. W. Hull, *Phys. Rev.*, **10,** 661 (1917); 17, 571 (1921); *Proc. Am. Inst. Elec. Engs.*, **38,** 1171 (1919); *J. Am. Chem. Soc.*, **41,** 1168 (1919).

light.   In thermophosphorescence kunzite exceeds all of the other minerals hitherto examined.   Well below 100° C. the intensity of light becomes much enhanced, at 125° it becomes a bright yellow, and at 200° a watch dial is well illuminated by the light from a small crystal.   If raised rapidly to 250° , the light is very brilliant, but becomes exhausted rapidly at this temperature, and drops to a much lower intensity with a reddish hue.   Apparently simultaneously with exhaustion of most of the light, the original lilac color is restored.   In fluorescence kunzite responds immediately to either penetrating or alpha rays from quite small quantities of radium and no marked change in fluorescence is observed as the coloring progresses.

From the standpoint of coloring, fluorescence and phosphorescence, kunzite is the most interesting of all minerals, and together with fluorspar and calcite forms a distinct class.

Calcite.—Different varieties of calcite showed the greatest differences in the properties of coloring, fluorescence, and of thermophosphorescence, which vary from complete absence to presence in marked degree.   Through the kindness of Prof. William P. Headden of the Colorado Agriculture College, we have had an opportunity of observing some of the effects in special specimens of calcite which he had collected.   Some of the varieties were colored yellow by 200 mgs. of Ra in the course of one to two months or by 150 millicuries of emanation in one to two weeks, when contained in rather large tubes.   The fluorescence of certain samples is marked under the influence either of alpha or penetrating radiation.   The color of fluorescence is a reddish orange and phosphorescence is very persistent at ordinary temperature.   The varying behavior of calcite is in marked contrast to the uniformity of kunzite as they came under our observation. The varieties of calcite which are active are quite comparable, however, with kunzite both in fluorescence and phosphorescence produced by radium radiation.

Sapphire.—Experiments have been carried out with 25 or 30 specimens of different colors and from various localities, including some synthetic ones.   All specimens were uniform in exhibiting no fluorescence, either to penetrating or to alpha radiation.   Thermophosphorescence was not observed in natural crystals, but was exhibited faintly by both white and pink synthetic crystals.   The thermophosphorescence was characterized by the relatively high temperature at which it appeared (above

150° C.) and at which it persisted (350° for a pink synthetic crystal). At 350° it was more brilliant than kunzite which had passed its maximum at a lower temperature and had dropped to a much fainter intensity. The thermophosphorescence of synthetic pink sapphire was red or orange-red, of synthetic white was yellow, which became paler with increasing temperature. Not a sufficiently large number of natural crystals was examined for thermophosphorescence to be sure that its absence is characteristic.

Change of color under radiation is general, but not universal. Colorless crystals either natural or synthetic are usually changed to golden or canary yellow in two to three days by the radiation from 200 mgs. Ra. Pink crystals either natural or synthetic were easily changed to a burnt orange color, probably corresponding to the addition of yellow to the original pink. Blue crystals change to a grayish or brownish green, without beauty or brilliancy, but the original color can be restored either by light or heat. Light yellow is usually deepened to a canary yellow, but may take green shades instead, which latter may also result in some cases from colorless specimens. In no case observed was the color produced light-permanent, resembling in this respect rock salt, kunzite, and fluorspar.

Ruby.—The color changes in ruby are not marked. Light colored natural ruby was not changed by radiation. Synthetic ruby was slightly darkened. Neither natural nor synthetic ruby showed any fluorescence under penetrating radiation, but showed a faint deep red fluorescence in emanation. Synthetic ruby showed a faint dark red thermophosphorescence at 150° C.

Emerald.—Neither natural nor synthetic emerald showed fluorescence under penetrating or alpha radiation; nor was change of color produced in any case. Synthetic emerald which had been exposed to 150 m.c. of emanation for ten days showed a faint green thermophosphorescence at 200° C.

Topaz.—Several different specimens of colorless topaz responded very uniformly to the penetrating rays from 200 mgs. Ra, though more slowly than rock salt, sapphire, and kunzite. In about a month a brownish amber color was produced which was uniform in all the specimens examined. Smoky topaz deepened in its own shade. The colors produced in topaz are apparently light-permanent. Neither fluorescence nor thermophosphorescence was observed.

Garnet.—Three specimens of deep red garnet acted uniformly in undergoing a reduction in color by the penetrating rays from 200 mgs. Ra, the color changing from deep red to violet, or purple. The color change produced is apparently light-permanent. No fluorescence nor thermophosphorescence was observed.

Quartz.—A fairly large number of specimens of different varieties of quartz was examined. In most cases the smoky color, characteristic of some varieties of natural quartz, is produced by radiation either from an initial colorless or by deepening a light smoky color or by changing the amethystine or rose color to smoky. A few failures to produce any color in colorless quartz by 200 mgs. Ra in one month were encountered.

In some cases radiation of light amethyst deepens the amethystine color, in other cases it changes to the smoky color. Continued failure to produce amethystine color in colorless quartz suggested the following test: A crystal of amethystine quartz was decolorized by heating in air to a dull red. After cooling, it was exposed to the penetrating radiation from 200 mgs. Ra which gradually restored the amethystine color, and after several months carried it to a much deeper amethystine shade than the original. While quartz is not fluorescent, either under penetrating or alpha radiation, most specimens show a marked thermophosphorescence of bluish-white or bluish-green shade, which is quite persistent and equal in brilliancy to that of fluorspar. Other specimens of milky quartz and amethystine quartz showed no thermophosphorescence following radiation, though both were decolorized under heating.

Tourmaline.—Two specimens of tourmaline, one pink, and one green, showed no change in color under penetrating radiation. The green tourmaline failed to fluoresce or to change color in ten days' exposure to an initial quantity of 150 millicuries of emanation, and later failed to show any thermophosphorescence up to 300° C. The pink specimen was examined only with respect to coloring by penetrating radiation.

Diamond.[5]—More than thirty specimens of cut diamonds, supposed to represent the principal diamond fields of the world, varying in size from a fraction of a carat to ten carats and in color from colorless to yellow and caramel brown, were examined. Fluorescence under penetrating radiation from a very thin tube

[5] For fuller details, see paper by the same authors which will appear in a later issue of this JOURNAL.

containing 60 mgs. Ra could not be detected. Fluorescent response to alpha radiation in the emanation tubes was universal and very sensitive. The color of the fluorescent light in emanation varied for different specimens from green to bluish-green to greenish blue to blue without any regularity with reference to the color of the diamond itself. For the same specimen the color of fluorescence varied somewhat with conditions as to intensity of radiation and gas pressure in the emanation tube (perhaps the latter only as effecting the former). Fluorescence was also observed near a thin alpha-ray bulb containing emanation.

Prolonged exposure (one month) to *penetrating rays* from 250 mgs. Ra failed to produce any change in color in five yellow Cape diamonds of four to ten carats. But prolonged exposure (45 to 75 days) to *alpha radiation*, either directly in 10 to 50 per cent. $RaCl_2$ salt or in emanation, produced universally a green color, which deepened with time (or with intensity of radiation) through grass green to a dark sage green. These results confirm that of Sir William Crookes[6] and met with no exception in all the more than thirty specimens treated. Colorless and yellow diamonds seem to take equally perfect green. Brown diamonds were off shade toward olive probably due to superimposed brown. The color is apparently light-permanent but can be discharged by heating to 450° C. for about an hour and in a shorter time at higher temperatures, or more slowly at lower ones. By interrupting the heating any intermediate shade of green can be obtained. The original color is finally restored by continued heating. The puzzling question as to the depth of the penetration of the colored layer, and the appearance in some specimens of "carbon spots" will be considered in the following paper devoted exclusively to the diamond.

Chrysoprase, opal and *other opaque minerals* showed no color change. This seemed to be a general characteristic of the opaque minerals. Upon heating chrysoprase after exposure to emanation, no light effects were observed, but a surface discoloration was produced which destroyed the natural lustre of the cut stone.

Aquamarine (light green), *zircon* (almost colorless), *peridote* (light green), and *moss agate* exhibited neither color change nor luminous phenomena. Aquamarine was exposed to penetrating radiation from 210 mgs. Ra for almost two years without changing hue in the slightest.

[6] Sir Wm. Crookes, *Phil. Tr. Roy. Soc* , **214A**, 433-45 (1905); *Sci. American*, Supplement No. 2270 (July 5, 1919).

Discussion of Results and Theory

The foregoing observations make no pretense to completeness, but are rather intended to show the complexity of the phenomena exhibited by the various transparent minerals and gems with respect to coloring and the emission of fluorescent and phosphorescent light, and to illustrate the difficulties that are encountered in attempting to propose a satisfactory theory. One is confronted with a most confusing complexity of relations and almost every possible combination is met. On the one hand, we have minerals like aquamarine and peridote which show a negative behavior throughout toward the radium radiations, being neither colored nor excited to any light emissions. Again, at the other extreme, we have a few minerals like kunzite and fluorspar which always exhibit in marked degree the phenomena under consideration. Among different specimens of the same mineral, we also have all extremes of behavior from complete regularity to almost complete variability. Such variable behavior has generally been regarded and, in the opinion of the writers, is properly regarded as pointing to the presence in certain minerals of *impurities* which are mainly responsible for their behavior during the following radiation. In those minerals, on the other hand, where no irregularity of behavior is observed, one is forced to the conclusion that the phenomena exhibited are due to properties inherent in the mineral itself.

That the presence of impurities, sometimes in minute quantities, plays a rôle in a variety of phenomena connected with coloring and light emission has been known for some time. It has been recognized in the case of phosphorescent alkaline earth sulphides, in the fluorescent-phosphorescent zinc sulphides, in the natural coloring of minerals, in the color produced in minerals by radiation, in the triboluminescence of natural zincblend (which must contain iron or manganese to show triboluminescence), and in many other related phenomena.

The following appeals to us as a simple and plausible general theory.[7] Certain groups of *electrons* are displaced by radiation from their normal positions and take up new metastable positions

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[7] The possibility of a theory based on a change in the mode of electronic "binding" (Bindungweise) was mentioned in the earliest paper of Meyer and Przibram (*Sitzb. Akad. Wiss. Wien*, **121**, IIa, 1416, (1912), but was not further elaborated nor mentioned in their subsequent papers.

among the atoms. No displacement (or only secondary displacement) of the atom is involved. No change in the crystal lattice as revealed by X-rays would be expected nor would there be any production of colloidal particles. One or more groups of electrons may be involved. By *group* is meant a number of electrons all having uniform positions in the original atoms from which they are displaced and taking after displacement uniform new positions among the other atoms.

In cases where two or more groups are involved, the return of one group to the original position may cause thermophosphorescent effects, the return of a different group may cause decolorization. This does not preclude the possibility that a single group may bring about both phenomena, thus rendering them absolutely coincident. On the other hand, the possibility is evident that the two may be entirely independent, each having a different energy index or either one may be entirely lacking, as we have shown to be the case for certain minerals.

Our assumption is that these electrons are removed by radiation to abnormal positions in which their constraints are lessened so that they vibrate with a frequency which may, and frequently does, fall in the visible region. Since the crystal is transparent the color complementary to the one absorbed by the electronic vibration is transmitted. In the metastable positions, under less constraint, the electrons are also freer to take part in electrical conduction and in photo-electric emission under radiative stimulus, and can also return to their normal positions under this stimulation or by that of heat.

Color-saturation would then be reached under continued radiation when the number of electrons returning to normal positions just equals the number being displaced. Upon cessation of radiation the electrons in abnormal positions may either remain indefinitely in the metastable position or may return gradually to their normal positions. The latter action will be brought about more rapidly by the stimulation of heat or some form of radiation of sufficient intensity to displace electrons from their abnormal positions without causing others to be driven from normal positions. One set of electrons may slowly revert, while another set remains indefinitely displaced.

The influence of impurities, in the light of this theory, may be one or both of the following: (1) To loosen electrons so that they

are more readily displaced. Again this effect may be due (*a*) to an effect exerted only on the electrons of the original atoms, or (*b*) by the formation of complexes from which the electrons are more readily displaced than from normal atoms. (2) The influence exerted by the impurities may be exerted on the electrons after liberation, in holding them more firmly in the abnormal positions, or both (1) and (2) may act jointly in some cases. The presence of an impurity may not be essential in all substances to the electronic displacements under consideration.

We can find in the present results very little support for the theory that colored minerals in nature have been colored by the action of the earth's radioactivity. If this were the case for diamonds, for example, we should expect to find in nature many *green diamonds*, since this has been shown to be the commonest (and in our experiments the only) color produced by radium radiation; but actually *green* is a very rare color in natural diamonds. Furthermore, the artificial colors, even when similar to the natural ones, appear to be much less permanent with respect to heat and often with respect to light.

On the basis of the present theory the actual proportion of color-producing electrons to the total number of atoms in a given slightly colored mineral must be quite small. It is calculated from ionization by penetrating radiation that the fraction in rock salt just noticeably colored is of the order 10^{-5}. Accordingly the quantity of energy necessary to produce (and even more so to discharge) color is surprisingly small in some cases. In general, it may be stated that the colors which are most easily produced are also most easily discharged and *vice versa*.

While it may be objected that the theory here proposed is not very definite and has not been quantitatively supported, it appears to us that it is capable not only of explaining the phenomena under consideration, but also has the necessary elasticity to fit the various other phenomena which are encountered and which must be explained. A more quantitative support must await a more intimate knowledge of atomic structure and of the properties of electrons and ions within that structure.