EFFECT OF HEAVY CHARGED PARTICLE AND FAST NEUTRON IRRADIATION ON DIAMONDS

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ABSTRACT

The color changes in diamonds produced by irradiation with high energy nuclear particles, neutrons, deuterons and alpha particles have been studied. The bombarding deuterons and alpha particles were accelerated to energies of 20 and 40 Mev, respectively, in the Crocker Laboratory 60-inch Cyclotron at the University of California. The permanence of the color under various conditions and the depth of the changes within the stone have been investigated. A summary of the work in this field together with a discussion of the results of this series of experiments will be presented.

Changes in color of a large variety of crystals have been reported as a result of exposing them to ultraviolet light, *x*-rays, cathode rays, and the radiations of radon and its decay products, which, of course, include alpha particles.[1,2,3] The information available from these sources is somewhat conflicting in character, particularly with reference to the variations in permanence of color changes produced in crystals of the alkali halides. This communication is primarily concerned with color changes produced in the diamond and accordingly color effects produced by ionizing radiation on other substances will be referred to but briefly.

The first report of induced color changes in crystals by irradiation with artificially accelerated, positively charged nuclear particles has been given by Cork.[4] His experiments included the bombardment of alkali halides, fluorite, quartz, beryl, and diamond, with 10 Mev deuterons produced by the cyclotron at the University of Michigan. The color changes produced in the alkali halides were similar to those reported by Bayley, though no comment was made in Cork's communication as to the degree of permanence of these changes. However, the observation was made that the color changes in the alkali halides disappeared upon heating to about 220° C. In the case of the diamond he made the observation that stones of an amber tint assumed a green coloration equivalent to that of the rare naturally occurring green diamond. It was stated that heating to approximately 900° C. for an unspecified period of time caused the green diamonds to revert to their

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[1] Goldstein, *Stiz. d.K. Akad. Wiss.*, Berlin, p. 937 (1894).

[2] Doelter, Das Radium und die Farben (1910).

[3] Bayley, P. L., *Phys. Rev.*, **24**, 495 (1924).

[4] Cork, J. N., *Phys. Rev.*, **62**, 80 (1942).

original color. Interestingly, a comment is made concerning the production of a color change in some of the stones which was bluish in character. No statement was made as to the number of stones irradiated or the specific conditions of the experiment, namely, the duration and intensity of the deuteron bombardment, or whether or not these bombardments were performed *in vacuo* or in the presence of air or some inert gas. A final statement is made that this transformation of color in the irradiated diamonds is presumed to be permanent at room temperature.

Green diamonds are known to occur naturally; however, diamonds of such a color which are of gem quality are extremely rare. For this reason, over a number of years, many attempts have been made to artificially produce this effect, usually employing radon as the source of irradiation. This procedure in the main was never very satisfactory for several reasons. First, such stones remained radioactive due to the presence of radium-D (Pb^{210}) which has a half-life of 22 years and which is a radioactive descendant of radon. In addition, radium-D has two radioactive daughters, namely radium-E (Bi^{210}) and radium-F (Po^{210}). It was a frequent misunderstanding that the stones themselves were made radioactive by treatment with radon, but actually the radioactivity was due to the deposition on the surface of the exposed stones of radium-D and its decay products. Inasmuch as the depth of penetration of the alpha particles from radon and its descendants was of the order of 2 microns, attempts to polish off the deposited radioactivity frequently resulted in the removal of the extremely thin superficial layer which had been subjected to alpha particle irradiation. Due to the fact that the associated beta particles and gamma radiation were not only less energetic but had far less specific ionization, their action was negligible in most instances.

Prior to the first reported irradiation of diamonds by high energy deuterons, some preliminary experiments of this character were carried on in 1941, using the cyclotron in the Department of Physics at Harvard University.[5] In these experiments small stones were used, again ranging in color from yellow to brown, which are commonly described as Cape stones. In these experiments 12 Mev deuterons were employed and the radiation was for three minutes with a beam intensity of 5 microamperes. At this point it is appropriate to indicate that deuterons in the energy range of 10 to 12 Mev can penetrate to a maximum depth of approximately 0.2 mm. or 200 microns, which is far greater than can be employed by using alpha particles from naturally occurring radioactive elements. In addition, the only appreciable residual radioactivity produced in stones by this type of irradiation was due to the presence of radioiso-

[5] Ehrmann, M. L., Unpublished data.

topes of nitrogen, the principal one being N^{13} with a half-life of 10 minutes. Obviously this radioactivity will diminish to the vanishing point after an interval of only a few hours. The question was raised as to the production of artificial radioactivity by this type of irradiation from the transmutation of elements other than carbon present in such diamonds. This is an insignificant factor for three reasons. First, these contaminating elements are present in very minute amounts, whose total is of the order of 0.01 per cent or less in stones which might be suitable for treatment by this process. Second, the volume of material irradiated was so small that only an extremely minute amount of foreign material would be exposed to the possibility of undergoing transmutation. Third, an investigation by spectrographic analysis at the Massachusetts Institute of Technology, revealed the presence of thirteen different elements. These were usually found in the following order of abundance: aluminum, silicon, calcium, magnesium, copper, barium, iron, sodium, silver, titanium, chromium, and lead. Aluminum, silicon and calcium were apparently present in almost all of the diamonds subjected to spectrographic analysis. Those diamonds which showed strong yellowish tints were observed to contain iron and titanium. The significance of the spectrographic analysis from the point of view of induced radioactivity is the fact that the two most commonly found foreign elements would result in the production of practically undetectable amounts of long-lived radioactivity as the result of the deuteron bombardment.

After it was discovered that the effect reported by Cork could be duplicated, larger diamonds were bombarded and in this instance a few white stones of gem quality, as well as stones possessing varying degrees of yellow coloration were included. In most instances all of the stones changed to the same tint of green except those that were initially of a fine white gem quality, and they became bluish green; those of a brown-color, became a dirty olive-green. It would seem probable that the last effect mentioned might be due to the combination of the original color of the diamond and having superimposed upon it the green changes produced by irradiation.

The diamonds which had been bombarded appeared to permanently retain their change in color, even when exposed for prolonged intervals to the sun or to artificial light at room temperatures. At this time it was also demonstrated that if the bombarded stones were re-cut to a depth greater than the range of the deuterons the green coloration was lost and the stone resumed its original color.

Recently at the University of California a series of detailed and more systematic experiments were conducted using the 60-inch Cyclotron at the Crocker Laboratory. Diamonds of varying sizes, ranging from $\frac{1}{2}$

carat to 30 carats, were employed. The majority of these were cut stones with either a brilliant or emerald cut. The colors ranged from small white stones of gem quality to those of quite dark brown. The bombarding particles were 40 Mev alpha particles, 20 Mev deuterons, and fast neutrons. A significant proportion of the fast neutrons possessed energies ranging from 10 to 20 Mev, the source being a deuteron bombarded beryllium target. A few of the diamonds were bombarded with deuterons and alpha particles within the evacuated target chamber; however, the majority of the stones which were exposed to alpha particles were mounted within a small chamber through which was passed a stream of helium. In this case the alpha particles entered the chamber after passing through a 0.001 inch aluminum foil which was used to maintain the vacuum within the cyclotron itself. The purpose of using alpha particles rather than deuterons arose from the fact that the amount of induced radioactivity in the aluminum mounts used to support the diamonds was very small as compared to that which would have been present if deuterons had been employed as the bombarding particles. This procedure made it possible to handle the aluminum mounts with safety a few minutes after the diamonds had been bombarded, thus permitting the treatment of a larger number of stones in the same length of time and the occasional re-irradiation of a stone necessary to achieve the desired degree of green coloration. The target mount which contained the diamonds was covered with a 0.00025 inch sheet of tantalum foil, the purpose being primarily to hold the stones in place during the irradiation.

The presence of an atmosphere of helium was found to be mandatory; otherwise, the diamonds would not turn green but rather appeared burned. It was observed that they turned golden, very dark yellowish, or brown in color. This was found to be superficial in character and usually corresponded to the maximum range of the alpha particles at this energy in the diamonds. The depth of penetration varied from 0.3 mm. to less than 0.1 mm. depending upon the orientation of the stone with respect to the alpha particle beam. This apparent burned appearance was interpreted as being due to the combined effects of (a) the stones were raised to a considerable temperature during the period of bombardment, (b) the presence of oxygen and nitrogen in the air, and (c) the oxidation of the tantalum foil.

After considerable preliminary experimentation it was found that the best results were achieved if the stones were bombarded for approximately 0.5 microampere hours with a beam current ranging from 5 to 10 microamperes. Inasmuch as the helium provided relatively little cooling, it was feared that the use of higher beam currents would be

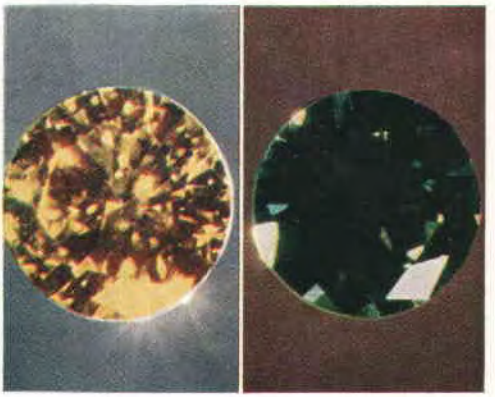

PLATE 1. A color photograph of a brilliant-cut diamond, weighing approximately 10 carats, before and after irradiation with alpha particles at an energy of approximately 40 Mev. The picture on the left indicates the appearance of the stone prior to irradiation, showing the characteristic yellow color of the gem. On the right may be seen the same stone after the alpha-particle irradiation.

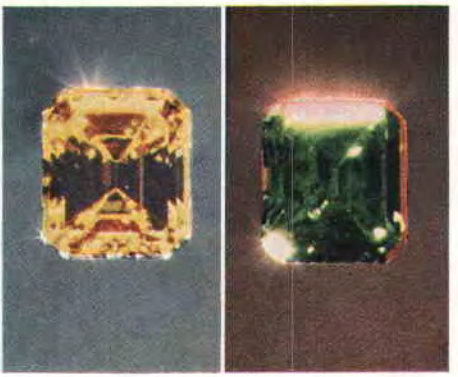

PLATE 2. An emerald-cut yellow diamond weighing approximately 8 carats before and after alpha-particle irradiation. As in Plate 1, the photograph on the left shows the stone prior to irradiation and that on the right, the same gem following irradiation, showing the characteristic green color associated with exposure of the diamonds to high energy alpha particles.

destructive, since the energy from the beam which would have to be dissipated as heat was considerable. The amount of heat varied depending on the size of the stone and since the intensity of the beam was not uniform, it also varied with respect to the position of the stone in the target mount.

As a first approximation, the energy dissipated from the beam was of the order of several watts per square centimeter. This may seem like a small amount but consideration must be given to the fact that the range of penetration was quite small. Thus this value of energy dissipation must be expressed in terms of watts per unit volume rather than watts per unit area. In this case the value is increased by nearly a factor of 100.

Most of the stones subjected to alpha particle bombardment were brilliant cut. They were usually irradiated only on the culet, since it was noted that this gave essentially the same results as stones irradiated both on the culet and table. Stones irradiated on the table alone showed a smaller color change, resulting in a very pale green. The effect of irradiating the stone on the culet alone is undoubtedly due to the many internal reflections within the diamond.

The effect of alpha particle irradiation did not appear to be significantly different whether the stones were large or small. The major difficulty encountered, apart from the accidental entry of air into the bombardment chamber, was that occasionally a stone appeared to have received an inadequate amount of bombardment. Under these circumstances, after allowing time for the decay of the short-lived radioisotopes of nitrogen and oxygen produced by the bombardment of the diamond, such a stone was re-irradiated.

As has been noted previously, these stones appeared to retain their color permanently, even under exposure to the sun as well as artificial light. Over a year has elapsed since the first stones were irradiated and these do not appear to have lost any of the original color. Heating the bombarded stones to 1000° C. for one hour in the absence of air will completely remove all of the green color and the diamond resumes its original color, with the exception that under such treatment the stone was usually slightly darker than before irradiation. Re-cutting the stones to a depth greater than the range of the alpha particle penetration completely returns them to the original color and none of the green tinge remains. This is a conclusive test for determining whether a green diamond has been artificially produced by heavy charged particle irradiation. In the case of neutron irradiation, as will be indicated later, the penetration is through the entire stone and re-cutting would not affect the color significantly. Since natural green diamonds have not been heated to a high temperature, the effect of this on the color is unknown,

and hence, heating a green diamond might not be conclusive proof as regards its origin of color. Uncut stones likewise turn green in color. This color is retained if the stone is cut in such fashion as not to remove too much of the area into which the alpha particles had penetrated.

On one occasion a number of cut stones were subjected to a prolonged fast neutron irradiation and turned a very pale green. This is assumed to be due to the fact that an insufficient amount of neutron exposure was achieved, since the total neutron flux integrated over the period of irradiation approximated 5×10^{16} neutrons per square centimeter.

The results described here, particularly the effects observed following the alpha particle irradiation of diamond, have demonstrated several facts. First, alpha particles, deuterons, and neutrons are capable of producing a greenish coloration of diamonds. Second, this effect is presumably permanent at room temperatures, even including circumstances under which such stones are directly exposed to sunlight.

Coloration of crystals, which has been alluded to briefly earlier, is believed to be due to the fact that under the conditions of exposure to appropriate irradiation, electrons are displaced from the lattice positions and lie in the space between. These isolated electrons possess the property of absorbing energy from visible light and this energy is then re-emitted at a fixed frequency from these electrons. The intensity of this re-emitted light will vary, depending upon the number of electrons displaced. For example, the irradiation of potassium chloride produces a characteristic bluish-purple color with either deuterons or alpha particles.[6] If the irradiation is sufficiently prolonged, the sample will appear almost black, whereas a pale bluish-purple color results with a relatively small amount of bombardment. In other words, the apparent effect of color change is not due to the difference in the frequency of light emitted but rather to an ever-increasing intensity due to more and more electrons being displaced which can absorb energy from other electrons which have received energy and are re-emitting it in the color characteristic for the particular crystal in question. In the case of the diamond, the same effect has likewise been observed, namely, if too much irradiation is given, the desired green color may become so dark as to give the stone a dark green appearance.

In the past it has been frequently thought that this green coloration was due to the interaction of the radiation with the contaminants within the diamond rather than to a change within the diamond structure itself. However, the available evidence strongly rules out the possibility that the green color is due to contaminants. A number of arguments

[6] Unpublished data.

may be presented to support this conclusion. The color change in stones ranging from pure white to the Cape stones of a relatively light yellow tint was always the same. Moreover, the amount of radiation required to produce this color effect at a level judged by visual observation did not vary by more than a factor of two. This variability lay within the range of experimental error, due to unhomogeneity of the beam intensity within the area in which the diamonds were bombarded. It is apparent that the amount or relative abundance of the foreign elements present will vary from diamond to diamond. This is a known fact, since these diamonds came from different regions in Africa and Brazil. Since over 200 diamonds were subjected to alpha particle bombardment and the regularities mentioned have prevailed, the possibility of the color change being due to foreign elements present seems exceedingly remote. Another consideration is the fact that these foreign contaminants are present in some instances in exceedingly minute amounts, this being particularly true of the white stones of gem quality. Upon this assumption the observed effect would be far too great to be accounted for on the basis of such minute amounts of other elements within the diamond. Finally, if the foreign elements had been a factor, then it would have been obvious that there would have been an extremely high degree of variability in response, both as to color and amount of radiation required to produce this effect. Representative illustrations of the effect produced by alpha particle irradiation are shown in Plates 1 and 2. The gem shown in Plate 1 was a brilliant-cut diamond weighing approximately 10 carats and the stone in Plate 2 was an 8 carat emerald-cut diamond. In both plates the photograph to the left shows the appearance of the gem prior to irradiation and to the right can be seen the effect of irradiation.

It has been suggested that effects of this character under the circumstances described above might be due to the physical displacement of carbon atoms within the lattice structure of the diamond. This concept does not appear to be reasonable on the basis of several lines of thought. The fact that heating to a relatively low temperature will destroy the green coloration of the diamond without destroying the diamond itself is a most cogent argument that the characteristic green color arises from electron displacement rather than displacement of carbon atom from the lattice structure. Another consideration is the fact that the number of electrons displaced either by direct ion bombardment or by the secondary effect produced by fast neutrons is presumably many thousand times greater than the number of carbon atoms displaced.

The effect of fast neutrons upon the diamonds is of interest, inasmuch as their range of penetration is far greater than the dimensions of not only the largest diamond irradiated in this series of experiments but any

known diamond. In the case of the neutron irradiation the direct mechanism for change in color is presumed to be somewhat different. The primary loss of energy when charged particles are employed, notably deuterons or alpha particles, is affected by the interaction of the charged particles with the electrons surrounding the carbon nuclei within the diamond. The neutron is an uncharged particle and does not interact with the electrons directly. The principal process by which the neutron dissipates its energy under these circumstances is the elastic collisions made with the carbon nuclei. Under such circumstances, for each collision approximately one-fifth of the energy of a neutron making such a collision will be imparted to the carbon nucleus. The carbon nucleus in turn will frequently then have imparted to it a kinetic energy of several million volts. When a carbon nucleus has received this amount of kinetic energy it will be knocked out of its position in the crystal lattice structure of the diamond and in the process will lose several of its orbital electrons. Thus, there is created within the diamond an ionizing particle, namely a moving, charged atom of carbon which in turn will dissipate its energy primarily by interacting with electrons of other carbon atoms until it comes to rest. Even though its range within the diamond will be less than 0.1 micron, it still passes by many billion carbon atoms. In short, the direct bombardment with charged particles such as deuterons or alpha particles or neutron irradiation produce the same effect, though in the case of the neutron it is of a secondary nature rather than primary; also it must be kept in mind that in the case of deuterons or alpha particles, the effect is superficial. While protons were not used it is predictable that such particles, where energy is of the order of 5 Mev or greater, would produce comparable effects. A review of the effects of radiation on various materials has been compiled by Slater.[7] A number of the factors that relate to the possible mechanism responsible for the green coloration of the diamond have been discussed in greater detail in his paper.

The use of deuterons, or alpha particles of sufficient energy to produce these color changes in the diamond which have been described may well produce various color changes in other precious and semi-precious stones. In this respect there is a limitation imposed upon most stones. It would be anticipated that stones which contain even minute amounts of water would be completely disintegrated, since there is an appreciable depth of penetration of these charged particles and the heat released within the range of penetration would be sufficient to disrupt the physical structure of the gem. A more attractive possibility in the case of

[7] Slater, J. C., *Jour. Appl. Phys.*, **22**, 237 (1951).

stones other than the diamond is neutron irradiation, since this can be conducted under conditions in which the heating effect can be reduced to a point where physical damage to the gem would not be anticipated.

Another limitation to the radiation of other precious and semi-precious gems by either charged particles or neutrons arises from the fact that there may be produced radioisotopes of quite an appreciable half-life and thus subject the stone to hazard. An example that might be cited is zircon, a semi-precious stone which contains a large amount of zirconium and a variable but appreciable amount of hafnium. The neutron irradiation of such stones would produce detectable amounts of radioisotopes of zirconium and hafnium which might prove troublesome. For example, Zr^{95} which is formed by the neutron capture of Zr^{94}, has a half-life of 65 days. Moreover, it decays to niobium-95 which has a half-life of 35 days. In the case of hafnium, the neutron capture of Hf^{180} results in the production of Hf^{181} with a half-life of 46 days. The problem becomes more complex with the use of charged particle bombardment as, for example, in the case of the alpha particle bombardment of zircon, radioisotopes of niobium, molybdenum and zirconium will be formed as well as radioisotopes of hafnium, tantalum and tungsten from the hafnium present. Before serious thought is given to a detailed study of affecting radiation charges for practical purposes in precious and semi-precious stones, the physical properties and chemical components, including foreign elements, should be known, for in a number of instances work of this character would be rendered impractical as has been described above. The use of very high energy accelerators in which protons, deuterons, or alpha particles may be accelerated to energy levels ranging from 200 to 400 Mev does not sound attractive, inasmuch as the beam currently available is relatively small, even though the energy is sufficient to penetrate large gems.

Acknowledgments

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