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# The deep blue Maxixe-type color center in beryl

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## Abstract

A deep-blue color center can be introduced into some beryl by gamma ray, X-ray, or neutron irradiation. If the original color is yellow or green, then a green or blue-green color can result from introduction of the same color center. This color center is characterized by: (1) strong dichroism with the intense optical absorption in the ordinary ray; (2) narrow band absorptions in the 5000 to 7000 Å region in the ordinary ray only; and (3) fading of this center on exposure to light or on heating to above 100°C. Very similar material, showing an absorption spectrum differing only in minor details, was found in Brazil at the Maxixe Mine about 1917, and the modern material has been named "Maxixe-type" beryl.

## Introduction

In 1917 a deep blue ("indigo," "cobalt," or "sapphire"-blue) beryl with properties quite distinct from those of aquamarine was found in the Maxixe mine in a 4–5 m deep pit some 50 m from the Piauhy River, southeast of Arassuahy, in northeastern Minas Gerais, Brazil. When it was discovered that the color faded on exposure to light, the mine was abandoned and the location has become lost. A brief report was given by Wild in 1932 and more details, including extensive refractive index data, were published by Schlossmacher and Klang and by Roebling and Tromnau, both in 1935.

When deep blue beryl (Crowningshield, 1972–73) having similar but not identical characteristics appeared recently in the jewelry trade, a detailed study of this material was undertaken. Deep green and blue-green forms also became available, and color illustrations have been published (Nassau, 1973; Nassau and Wood, 1973), the latter showing the better color reproduction of the two.

## Experimental

Samples of current deep blue and deep green material were obtained by courtesy of Mr. R. Crowningshield of the Gemological Institute of New York City, Mr. H. Rubin of the Gemset Company of New York City, and Dr. E. Gübelin of Lucerne, Switzerland. A fragment of the 1917 Maxixe Beryl, which had been kept in the dark since that time, had been given by Mr. F. Quast of Idar-Oberstein to G. O. Wild (Wild, 1933) and thence to Mr. B. W. Anderson of the Laboratory of the London Chamber of Commerce, who kindly permitted us to use part for experimentation.

A total of 235 specimens of pale-colored beryl were also tested for their susceptibility to gamma rays in developing this color center. These specimens included a number of those used in previous studies (Wood and Nassau, 1967, 1968) as well as others from a variety of locations, mostly in Brazil.

In Table 1 are listed the original 1917 Maxixe specimen, the 31 specimens which showed a deep blue or green Maxixe-type spectrum as we received them, and eight additional beryl specimens in which we were able to develop deeply colored Maxixe-type spectra. A further 25 beryl specimens showed noticeable, but only weak, spectra of this type after irradiation and are not listed; the remaining 170 specimens showed no noticeable change.

Samples were cut and polished with the hexagonal axis in the plane of the specimen. Polarized absorption spectra were recorded on a Cary Model 14 spectrophotometer in the range from the absorption edge near 2000 Å out to 25,000 Å. Absorption data for faceted gemstones were taken with the stones immersed in carbon tetrachloride in a fused silica cell to reduce refraction at the facets. Samples were kept in the dark when not being examined, and the brief light exposure in the dispersed radiation during absorption measurements was insufficient to cause significant bleaching.

Irradiations were carried out with gamma rays in a Cobalt-60 cell at 0.70 megarads per hour. Neutron irradiation was carried out in the Brookhaven reactor at $10^{13}$ fast neutrons plus $10^{12}$ slow neutrons per $cm^2$ per second. X-ray irradiation was effected with a

TABLE 1. Maxixe and Maxixe-Type Specimens Used in This Study

Maxixe and Maxixe-Type Specimens
Used in This Study

| Designation | Type* | Origin* | Color When Bleached | Alkali Content |
|---|---|---|---|---|
| | | A. Maxixe or Maxixe-Type as Received | | |
| 589 | G-MT | Br? | yellow** | Medium |
| 590 | G-MT | Br? | pale yellow | Medium |
| 591 | B-M | Brazil 1917 | colorless | High |
| 592 | B-MT-Gem | Br? | pale pink | Medium |
| 593 | B-MT-Gem | Br? | pink | Medium |
| 594 | B-MT | Br? | pale pink | High |
| 611 to 613 | B-MT-Gems | Br? | pale pink** | Medium to High |
| 618 to 638 | B-MT-Gems | Br? | pale pink** | - |
| 639 to 641 | G-MT-Gems | Br? | yellow** | - |
| | | B. Aquamarine, Morganite, Golden or Colorless Beryl with Maxixe-Type Precursor | | |
| 446*** | B-MT | Brazil | colorless | Low |
| 447*** | G-MT | Brazil | yellow | Low |
| 480*** | G-MT | North Carolina | pale aqua green | High |
| 506*** | B-MT | Unknown | pale aqua blue | Medium |
| 596 | BG-MT | Br? | pale yellow | Low |
| 597 | BG-MT | Br? | yellow | Low |
| 598 | BG-MT | Br? | deep yellow | Low |
| 599 | B-MT | Br? | pink | High |

* B-Blue, G-Green; M-original 1917 Maxixe, MT-Maxixe-Type; Gem-faceted gem stone (5 to 8 carats in size), all other specimens are crystals or fragments of crystals; Br? probably from Brazil or said to be from Brazil.

** Not bleached; color deduced indirectly from examination of the extra-ordinary ray color.

*** Previously studied by Wood and Nassau (1967, 1968); note that #447 was erroneously listed as #477 in Table 1, Section 2e of Wood and Nassau (1968).

tungsten target tube operated at 25 kV and 35 mA at a distance of 3 cm.

For the heat-fading experiments, small slabs (3.2 mm × 5 mm × 10 mm) of specimen #446 were introduced into an air oven at various temperatures in contact with a previously equilibrated brass block with a thin layer of silicone lubricant for good thermal conduction. The heating was continued for various periods of time. Light bleaching was achieved either by placing the sample 15 cm from a standard 100 watt tungsten filament lamp bulb, or by taping the specimen to a south-facing glass window in daylight. We were careful to avoid heating the samples to more than 50°C during the light bleaching experiments.

Induced radioactivity was measured by gamma-ray spectrometer using a Li drifted Ge detector and a 1024 channel analyzer.

## Comparison of Maxixe-type beryl with aquamarine

Polarized absorption spectra in the 2000 to 8000 Å region are shown in Figure 1 for blue and green aquamarine beryl, for the 1917 Maxixe specimen, and for current blue and green Maxixe-type material as received for study. We designate the characteristic narrow band spectrum at 5000 to 7000 Å as "Maxixe" for the original 1917 beryl from the Maxixe mine, but "Maxixe-type" for the closely related but slightly different spectrum seen in specimens #590 and 592. The difference between the blue and green specimens of both aquamarines and Maxixe-type beryls lies in the position of the $Fe^{3+}$ absorption edge (Wood and Nassau, 1968), being above 4000 Å in green specimens but below 4000 Å in blue specimens. Chemical analyses show that the iron content in the green Maxixe-type specimens is very much higher than in the blue material. Table 2 shows very clearly this difference in iron content between the green specimens 589 and 590 and the blue specimens 591 and 594. The characteristic line absorption between 5000 Å and 8000 Å, however, is the same in both blue and green Maxixe-type material. Blue maxixe and Maxixe-type specimens showed very low concentrations of transition metals, particularly iron (0.01 percent or less Fe—Table 2); iron had been reported to be absent by Wild (1933) and at the 0.03 percent level by Roebling and Tromnau (1935). They did not detect any cobalt and neither did the present analysis, thus eliminating Wild's suggestion that this might cause the blue color. It may be concluded that the narrow band absorption features in the 5000 to 7000 Å region cannot be attributed to iron or any other transition element.

There are some differences in the narrow band absorption features between the 1917 Maxixe specimen and the Maxixe-type specimens of current material. The differences are more distinct when specimens are cooled to near liquid helium temperature because the line widths are significantly reduced (Fig. 2). The location of band maxima for both room temperature and 10°K are given to the nearest 5 Å in Figure 2. The room temperature absorption wavelengths in Maxixe beryl are consistent with those observed by Wild as quoted by Anderson (1956). These absorptions occur only in the ordinary-ray spectrum in both Maxixe and Maxixe-type samples, and their presence provides the most reliable test for distinguishing Maxixe-type material from aquamarine.

Another test is based on the opposite dichroism of the two materials. The blue color of aquamarine is usually carried by the extraordinary ray, while that of Maxixe-type beryl is carried by the ordinary ray. It is

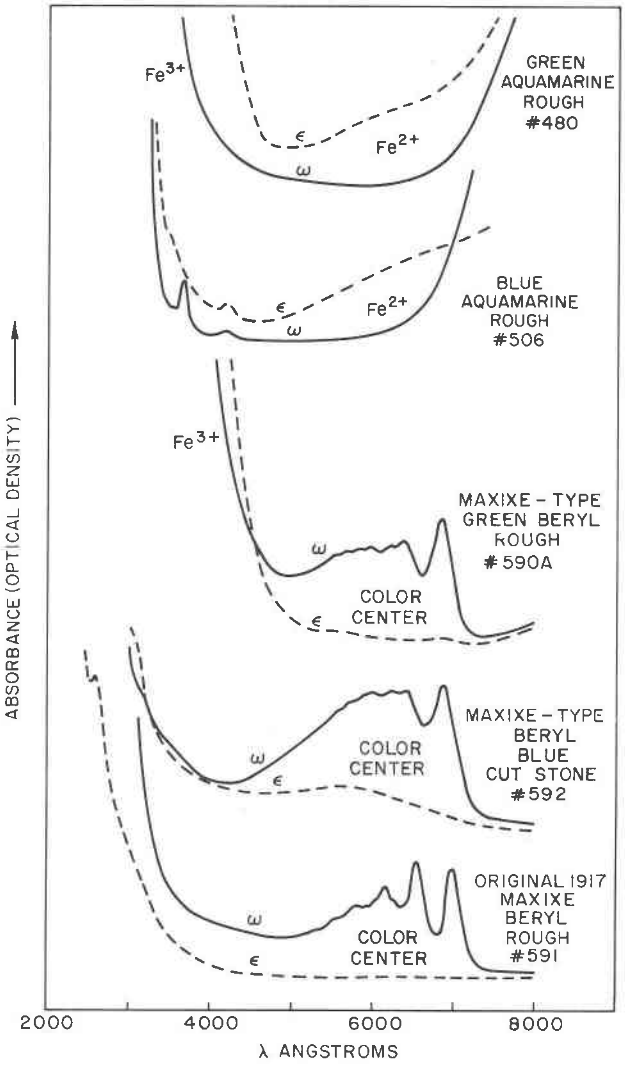

FIG. 1. Spectra of Maxixe-type beryls and aquamarines; ω is the ordinary ray spectrum, ε the extraordinary ray spectrum. Absorbance = $\log_{10}(I_0/I)$.

TABLE 2. Chemical Analyses

| Sample # | 589 | 590 | 594 | 591 |
|---|---|---|---|---|
| Type | Green Maxixe-Type | Green Maxixe-Type | Blue Maxixe-Type | Original 1917 Maxixe |
| a) Semi-Quantitative Spectrochemical Analysis | | | | |
| Major (>1%) | Si,Al,Be,Mg | Si,Al,Be,Mg | Si,Al,Be,Mg | Si,Al,Be,Mg |
| 0.X% | Fe,Li | Fe,Li,Sc | Sr,Cs,Na | Sr,Cs,Na |
| 0.0X% | Mg,Na | Mg,Na,Mn,Zn | Mn,Ag,K,Li,Fe | K,Li |
| 0.00X% | Ag,K,Mn,Sc,Zn | Ag,K,Cu | Mg,Rb | Fe,Rb |
| 0.000X% | Cu,Ca,Cs | Ca,Cs | Ca,Cu,Pb,Ba | Ca,Cu,Mg,Pb,Ag,Ba |
| b) Quantitative Analysis | | | | |
| Fe | 0.17% | 0.25% | 0.010% | 0.005% |

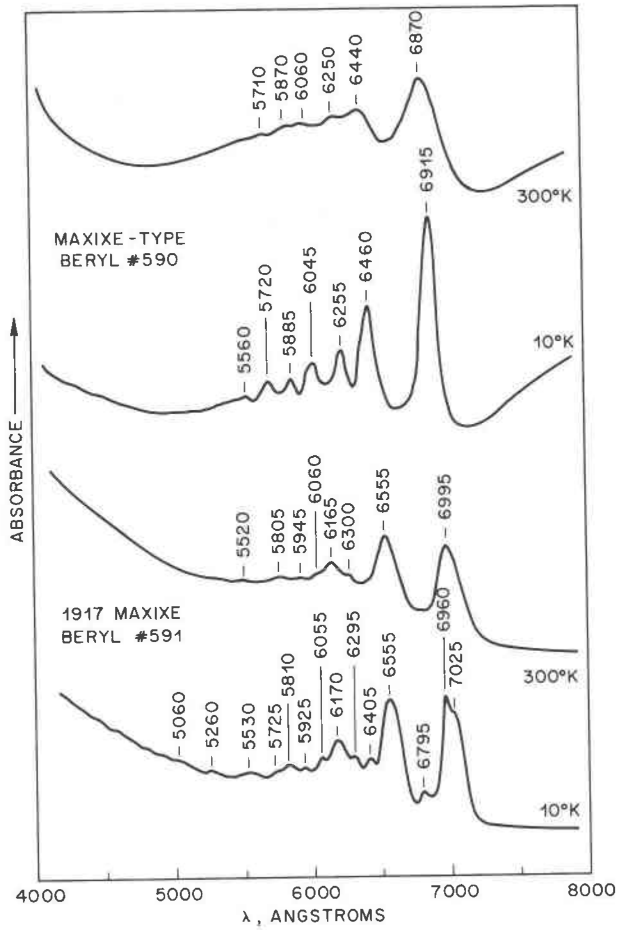

FIG. 2. Spectra of Maxixe and Maxixe-type beryl, ordinary ray, at 300 K and 10 K.

difficult at times to apply this test to aquamarines, particularly to pale green ones, but the absorption causing the intense blue components of color in Maxixe-type material is always carried by the ordinary ray.

No Maxixe-type optical absorption was found in our previous study of 79 beryl crystals from various localities, and none has been reported in the literature since the early reports on the 1917 material published in the 1930's. Its rarity, and the sudden flood of material recently, has lent considerable weight to the initial hypothesis that irradiation was involved in its production.

### Bleaching and irradiation experiments

A green Maxixe-type specimen was subjected to the series of experiments summarized in Figure 3. In the bottom curve (a) is shown the spectrum of the material as received. After heating to 200°C for 1/2 hour, the sharp line spectrum disappeared (b), and on further heating to 400°C for a half-hour the absorption edge near 4000 Å was shifted toward shorter wavelength (curve c). We could then restore the sharp line spectrum reversibly in the heat-bleached material by any of three irradiation treatments. Curve (d) shows the spectrum after $Co^{60}$ gamma-ray treatment (29 hours = 20 megarads); curve (e) after X irradiation (24 hours, 30 kV, 35 Ma, 3 cm distance); and curve (f) after neutron irradiation (5 min = $3 \times 10^{15}$ neutrons/cm$^2$). Curve (g) shows the bleaching of the sharp line spectrum with daylight. Here some of the material as received—*i.e.*, having the absorption shown in curve (a)—was exposed in a south window for one week to daylight with sun, whereupon it lost the characteristic Maxixe-type absorption.

A similar set of experiments was carried out with a

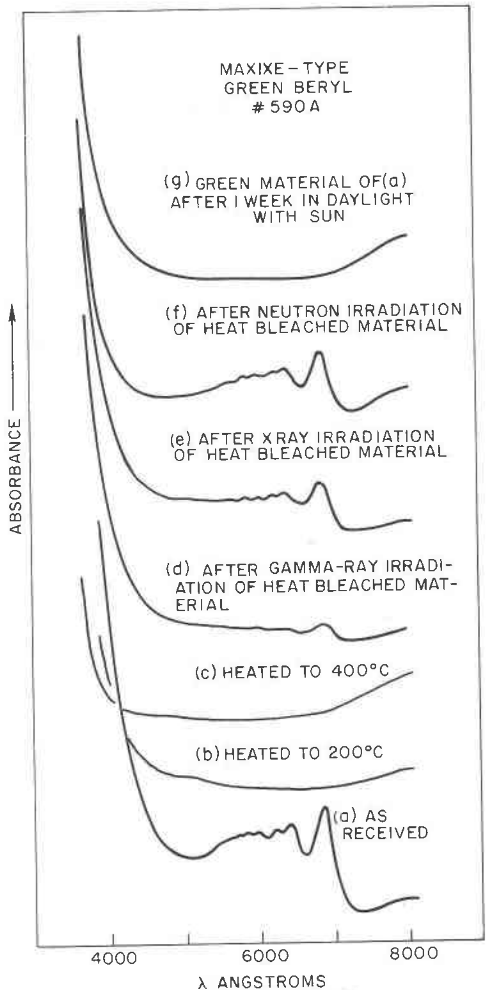

FIG. 3. Spectra of green Maxixe-type beryl showing the effect of light, heat, and irradiation; ordinary ray.

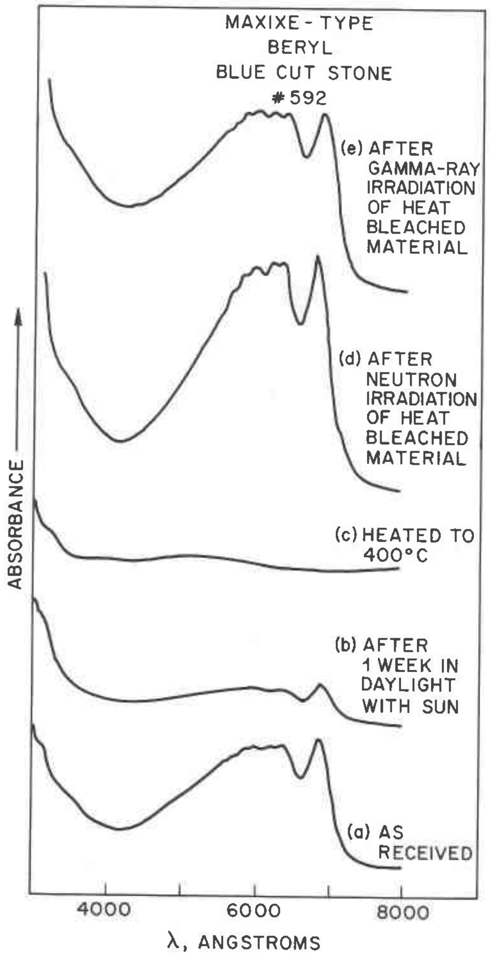

FIG. 4. Spectra of blue Maxixe-type beryl (cut stone immersed in carbon tetrachloride in quartz cell) showing the effect of light, heat, and irradiation; ordinary ray.

deep blue faceted stone, and the results are shown in Figure 4. In this case the neutron and gamma ray irradiations were longer (15 min — $10^{16}$ neutrons, and 12 days = 200 megarads $Co^{60}$). The fading from exposure to one week of daylight with sun (shown in curve (b), Fig. 4) was similar to that from exposure at room temperature to a 100 Watt tungsten filament light at a distance of 15 cm for two weeks. The results from the green material and the blue material are very similar, the principal difference between the two being the position of the short wavelength absorption edge.

From the absence of transition element impurities, the ease of decoloration with light or heat, and the recoloration with a variety of penetrating radiations, we conclude that a color center is the cause of the Maxixe-type optical absorption features. Andersson (1974) has studied a blue Maxixe-type beryl and a similarly colored irradiated beryl (initially pink) by paramagnetic resonance techniques, and suggests that trapped hydrogen may be involved in the formation of the color center. He did not, however, investigate the question of whether the center he studied was responsible for the optical absorption or merely associated with it, and further work seems to be required on this point.

There appears to be no direct correlation between the occurrence of the Maxixe-type color center and the alkali content of the crystal. In previous reports we have shown that a rough estimate of the total alkali content of beryl can be derived from the intensity of the infrared absorption between 1 $\mu$m and 2 $\mu$m due to water associated with alkali (Wood and Nassau, 1967, 1968). The alkali content of 17 of the specimens listed in Table 1 was estimated this way, and is given in the last column in the table. From the fact that, for example, #446 has low alkali (~ 0.01%) but is fairly strong Maxixe-type, while #594 has high alkali (~ 0.5%) and about equally strong Maxixe-type, we conclude that alkali is not involved in the color center directly. The original 1917 Maxixe specimen was high in alkali content (~ 0.5%).

The process of the formation of the color center during gamma irradiation was followed by measuring the specific absorbance ($\alpha = 1/l \log_{10} I_0/I$, $l$ being the

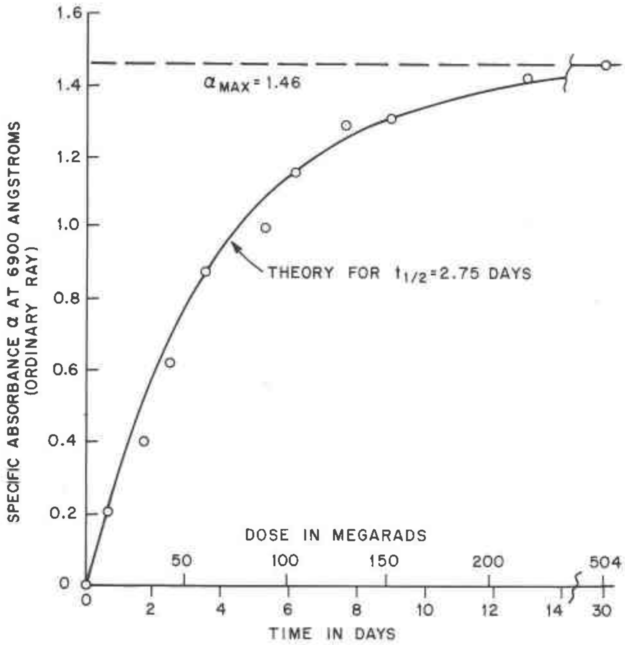

FIG. 5. Development of Maxixe-type blue color in beryl #446 during gamma-ray irradiation; points experimental, line theory.

TABLE 3. Gamma Ray Coloration Rate Parameters for Maxixe-Type Beryls

| Specimen Designation | Saturation Coloration $\alpha_{max}$ at 6900 Å | Half Coloration Time $t_{1/2}$ days | Half Coloration Dose $d_{1/2}$ megarads |
|---|---|---|---|
| 446 | 1.46 | 2.75 | 46.2 |
| 596 | 1.93 | 4.0 | 67.2 |
| 597 | 1.92 | 4.2 | 70.6 |
| 598 | 2.22 | 6.0 | 100.8 |

thickness in cm) at 6900 Å in the ordinary ray as a function of irradiation dosage. The calculated curve which best fits the experimental points in Figure 5 is computed using the saturation value of $\alpha_{max} = 1.46$ and a half coloration time $t_{1/2} = 2.75$ days (or half dose $d_{1/2} = 46.2$ megarads) in the exponential coloration expression:

$$\log_{10}\frac{\alpha_{max}}{\alpha_{max}-\alpha} = 0.301t/t_{1/2} = 0.301\ d/d_{1/2},$$

where $\alpha$ is the specific absorbance at 6900 Å after $t$ days (or $d$ megarads) of gamma ray exposure.

This behavior is indicative of a single type of coloration process in which the rate of development of color centers is proportional to the number of precursor centers remaining to be converted to color centers. It shows that only a fixed amount of the color center precursor is present in the material. Different specimens showed not only different saturation colorations due to different precursor concentrations, but also different half coloration times, indicative of different absorption cross-sections for the gamma rays (Table 3).

The blue irradiated material showed a slightly smoky color, and heating to as little as 100°C for a few minutes removed this smoky hue. Although readily seen by the eye, this change was not sufficiently large to be visible in the absorption spectrum and was not further investigated.

The process of the heat-induced decoloration of the Maxixe-type feature (in the absence of light) was studied at various temperatures, as shown in Figure 6 where the fraction remaining of the original color is plotted against time at the elevated temperatures. A temperature even as low as 125°C gave a rapid initial bleaching followed by a much slower stage, a behavior indicative of a process involving more than one mechanism. At 200°C rapid fading was almost complete in 30 minutes. An attempt was made to fit the curves of Figure 6 to exponential components; in the case of the 164°C a good resolution into components with half lives of 10 min and 96 min was obtained (Fig. 7). However, unambiguous resolutions could not be achieved at the other temperatures, and it was therefore not possible to obtain activation energies for the decoloration processes.

Gamma irradiation produced a number of changes in features of the absorption spectra other than the Maxixe-type bands. The heat-induced conversion of green beryl to blue beryl (commonly used to improve the value of aquamarine) by the shift in the absorption edge near 4000 Å to shorter wavelength was reversed by the various irradiations used. The change on heating is due to the conversion of $Fe^{3+}$ in the octahedral Al site (yellow) to $Fe^{2+}$ (colorless) (Wood and Nassau, 1968). Irradiation reverses this change, as can be clearly seen in Figure 3.

Another set of changes was seen in the water absorptions lines, a number of which were intensified by irradiation. As one example, the $\omega$ spectrum line at 13,900 Å (7,200 $cm^{-1}$ in Figure 3 of Wood and Nassau, 1967) increased from $\alpha = 0.26$ to $\alpha = 0.56$ on $\gamma$-ray irradiation, and reverted to $\alpha = 0.38$ on heating for five hours at 250°C. Other lines which increased were in the $\epsilon$ spectrum at 22,260, 22,590, 22,720, 23,640, and 23,760 Å. We have not studied this phenomenon in detail, but it does not appear to be related to the formation of the Maxixe-type color center.

Immediately after neutron irradiation of specimens #590 and 592, considerable induced radioactivity was

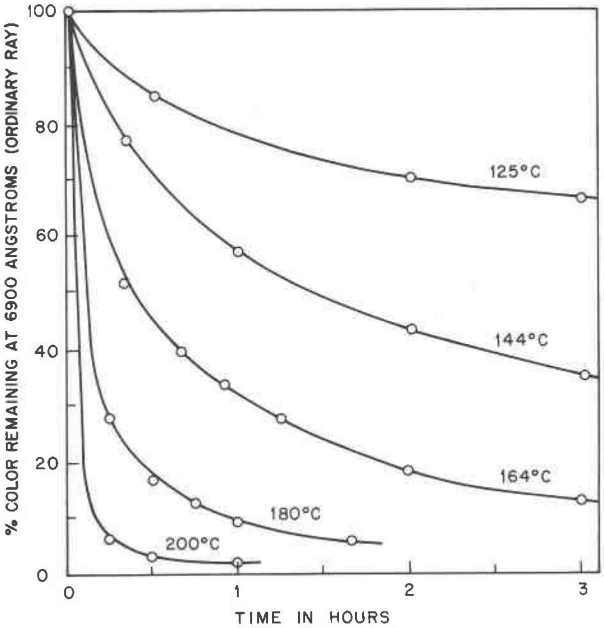

FIG. 6. Loss of Maxixe-type blue color in beryl #446 on heating at different temperatures; percent color = 100 $\alpha/\alpha_0$.

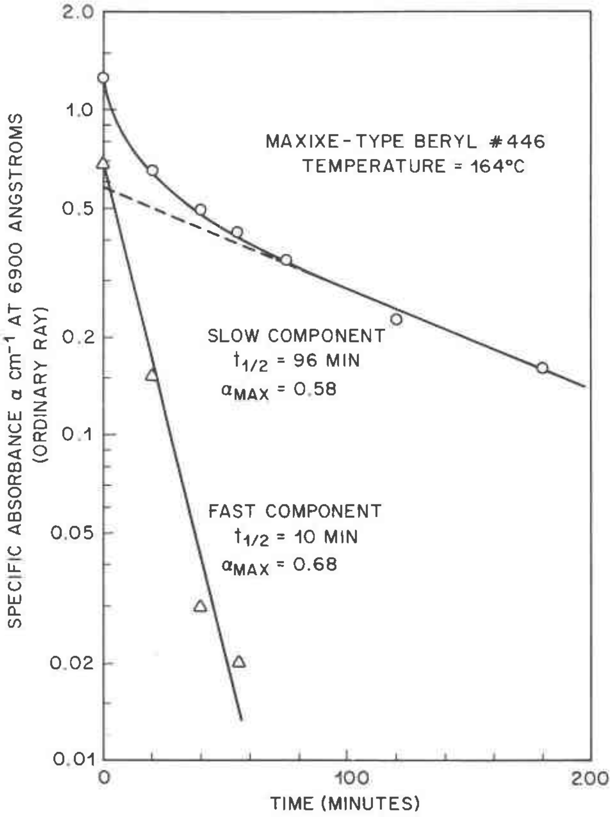

FIG. 7. Decomposition of the 164°C heat-bleaching curve of Figure 6 into two exponential components; points experimental, lines theory.

present. After one week the only abnormal radioactive species revealed by gamma-ray spectroscopy in both samples was cesium-134, which does not occur in nature, and has a half-life of about two years. It is a result of neutron capture by the cesium-133 commonly present in small quantities in much beryl (Deer, Howie, and Zussman, 1962). A check of all the other specimens of Table 1 in the as-received condition indicated that three of the deep blue faceted gem stones had a low level of cesium-134 radioactivity (about 3 × $10^{-3}$ microcuries in specimens #618, 629, and 638). Accordingly it is clear that some of this material had definitely been neutron irradiated; it is possible that some or all of the rest may have been irradiated with gamma-rays, X-rays, or other suitable treatment to develop the Maxixe-type color, since these treatments leave no other evidence of their use. That this material did not come from the Maxixe mine is established by the differences in the spectrum as seen in Figure 1.

A recent account (Bastos, 1975) states that Maxixe-type beryl can be made from pink beryl (morganite) mined in Barra de Salinas, Minas Gerais, Brazil, but the process was not disclosed. Guso and Williams (unpublished; Argonne National Laboratory) have irradiated six colorless beryls from Rhodesia and also obtained deep blue material which faded rapidly.

We have found that the original 1917 Maxixe beryl also faded rapidly on heating or on exposure to light (Fig. 8). Here again irradiation resulted in the reformation of the blue Maxixe color center, but in addition the absorption edge at 4000 Å also shifted, resulting in a green color. It is not clear if the valence change of the iron ion at the low level present in this crystal is adequate to account for the absorption edge shift. It should be noted that even the relatively pale blue color initially present was not completely restored by 15 minutes of neutron irradiation (Fig. 8) so that apparently this material has a low absorption cross-section for the Maxixe color center, but a high

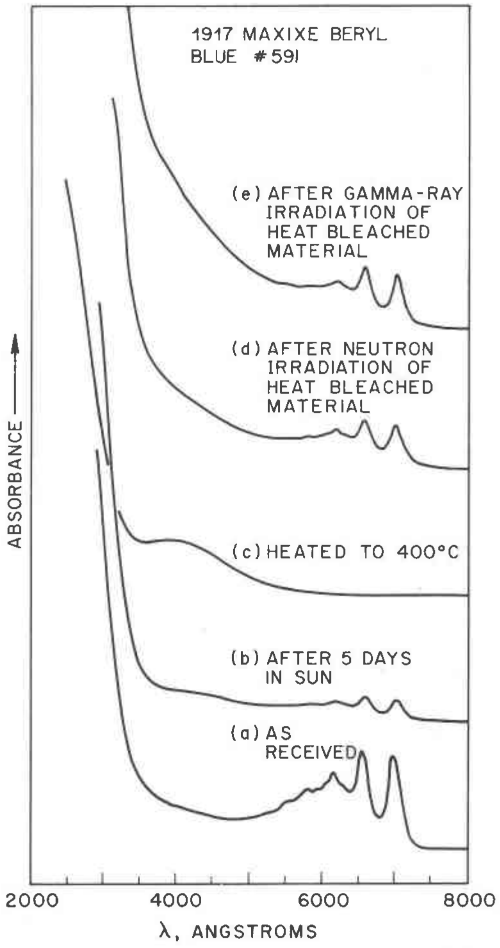

FIG. 8. Spectra of 1917 Maxixe beryl, showing the effect of light, heat, and irradiation; ordinary ray.

cross-section for the reaction producing the edge shift.

What can be deduced, however, is that geological irradiation since the time of formation could not have caused the blue Maxixe color center, since it would also have produced a green color due to the presence of the yellow component (indicated by the short wavelength absorption edge near 4000 Å). Irradiation plus subsequent heating could not have produced the blue color of the original Maxixe either, since the blue color center bleaches at a lower temperature than that required to remove the yellow component by a shift of the absorption edge (see also Fig. 3). Accordingly it would appear that the Maxixe color center as seen in the 1917 beryl specimens from the Maxixe mine must have been formed during the geological growth process by a specific set of growth conditions and not natural irradiation. No information is available concerning the nature of these conditions.

## Summary

A deep blue color center is produced in beryl by a variety of penetrating radiations. If the original beryl is yellow or green, the resulting color can be a green or blue-green. This color center cannot be induced in just any beryl, and the nature of the required precursor is presently unknown. It does not appear to involve transition metals, alkalis, or water.

The color center is best characterized by the narrow absorption bands in the ordinary ray only, giving a quick test by examination in polarized light. Two variants exist. One, termed Maxixe, is found in the original 1917 Maxixe material which occurred naturally. The second, termed Maxixe-type, can be produced in a significant fraction of irradiated beryls of random origin, and there is here no clear evidence for a natural occurrence.

Both light and heat exposure can cause a complete fading of the blue component of the color, and it can be again restored by $\gamma$-ray, X-ray, or neutron irradiation in the Maxixe-type material. In the case of the initially blue 1917 Maxixe material, irradiation of the bleached material produces a green color, indicating that irradiation did not produce the Maxixe color center in nature but that it was formed in some other way during the growth process.

## Acknowledgments

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