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Ferrous and Ferric Ions in Synthetic α-Quartz and Natural Amethyst

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Abstract

The generation and the removal of the various optical absorption bands in natural amethyst and in synthetic α-quartz doped with either Fe^{2+} or Fe^{3+} ions has been surveyed. Positive rhombohedral growth regions of synthetic α-quartz containing Fe^{3+} ion proved to be related to the generation of the amethyst color upon treatment with ionizing radiation. It is believed that the interstitial Fe^{3+} ions in voids perpendicular to positive rhombohedral faces furnish charge compensation for substitutional Fe^{3+} ion. This combination is the precursor of several color centers responsible for the production of the amethyst color.

Introduction

Iron Centers in Amethyst

Many early authors (Woodward, 1729; Hauy, 1817; Marx, 1831)[2] attributed the amethyst color in α-quartz to iron. In his classical study, Holden (1925) found that iron is always present in amethyst and reported an absorption maximum in the region of 5300–5400 Å. Frondel (1962) observed that in some instances the colored faces of amethyst are selectively filmed by finely divided iron oxide. Cohen (1956) summarized the different possibilities for the state of the impurity atoms responsible for the violet color in amethyst.

From EPR studies of natural amethyst and citrine, Hutton (1964) concluded that the presence of iron alone is not sufficient to develop the violet color of amethyst and that high-energy radiation is also necessary. This supports the early view of Berthelot (1906) and also provides one possible reason for the lack of quantitative correlation of color with iron content. Paramagnetic resonance investigations by Barry, McNamara, and Moore (1965) suggest that precursor centers arise from the substitution of Fe^{3+} for Si^{4+} in the quartz structure. The charge neutrality is usually achieved by the presence of an interstitial alkali-metal ion on the center's two-fold axis. Further EPR studies by Lehmann and Moore (1966b) revealed several Fe^{3+} precursor centers.

The similarity of several of the color centers to iron (Fe^{2+} and Fe^{3+}) optical transitions strengthens the belief that most of the optical bands characteristic of natural and synthetic amethyst (Schlesinger and Cohen, 1966) result from iron impurities.

Using X-ray absorption topographic techniques, Schlössin and Lang (1965) measured local differences in iron concentration which they correlated with the pattern of imperfections in an amethyst crystal. A periodic distribution of dislocations was associated with repeated twinning on the position rhombohedral faces (r). In the relatively more perfect negative rhombohedral (z) growth sectors, dislocations were marked by faint wispy lines. Not only did iron in the r sectors exceed that in the z sectors, but Schlössin and Lang also found that the iron content in the Dauphine-twinned regions of r sectors was below the average for the sector.

The present paper is mainly concerned with the nature of some of those centers related to iron in both natural amethyst and synthetic α-quartz.

Experimental

Materials

The natural quartz investigated was a Brazilian amethyst crystal (Sample R-1454) obtained from the Mineralogy Branch of the National Museum of Natural History, Washington, D. C. The sections studied were cut from the deeply amethyst-colored

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[2] A detailed review of the properties of amethyst is given by Frondel (1962).

TABLE 1. The Major Absorption Maxima in a Natural Brazilian Amethyst*

Band	Reference	Position of (eV)	Band maximum (A)
α	Hassan (1970)	6.2	2,000
β	Cohen (1956)	5.6	2,250
ξ	Arnold (1955)	$\sim$3.5	$\sim$3,570
η	Hassan (1970)	$\sim$3.0	$\sim$4,100
Θ	Vedeneeva (1940)	$\sim$2.3	$\sim$5,450
κ_{complex}	Hassan & Cohen (1969)	$\sim$1.3	$\sim$10,000

* *Smithsonian Institution No. R-1454.*

portions (rhombohedral growth regions) of the crystal.

The synthetic quartz crystals grown and presented for our study by Sawyer Research Products, Inc. of Eastlake, Ohio included:

(1) A light brownish-yellow α-quartz grown on a seed cut perpendicular to the *c* axis (*z*-growth) with iron impurities incorporated mainly as Fe^{3+} (Sawyer Crystal number Y-5). Although the color appeared to be homogeneously distributed in hand specimen, striations of color parallel to the *c* axis were observed on polished thin sections of the crystal.

(2) Green α-quartz (Sawyer number A-84) grown like the first but mainly with Fe^{2+} ion and some Fe^{3+} as impurities. The colored striations parallel to the *c* axis ranged from green (due to Fe^{2+}) to brown (due to Fe^{3+}).

(3) Synthetic Fe^{3+}-doped quartz, faint yellow in color, grown on a positive rhombohedral seed plate (Sawyer number H-95) from a solution similar to that of specimen 1 (Sawyer, personal communication, 1970). Growth in this orientation produces iron-related color centers in the visible region of the spectrum (Tsinober and Chentsova, 1959).

Details of sample preparation and optical absorption measurements are described in the preceding paper (Hassan and Cohen, 1974).

X-Irradiation Experiments

X-irradiation experiments were performed in a Picker Industrial X-ray unit. The X-ray tube is a water-cooled Machlett AEG-50-T type with a tungsten target and a beryllium window. The irradiations were carried out 5.4 cm from the beryllium window at room temperature and at tube settings of 45 pkV and 35 mA.

Bleaching Experiments

The specimens were illuminated with the high intensity output of a high pressure Hg,Xe lamp whose output peak intensity falls in the 2537 Å region.

In the heat treatment the specimens were heated in air for 2 hours at intervals of 25° until complete oxidation of Fe^{2+} to Fe^{3+} occurred. The temperature was measured by a ($Pt_{90}Rh_{10}$) thermocouple placed in contact with the specimen during heating.

Iron Centers in α-Quartz

Optical Absorption Spectra

The absorption spectra of differently oriented sections of natural amethyst and of synthetic α-quartz doped with either Fe^{3+} or Fe^{2+} were measured at room temperature using normal light. Table 1 summarizes the main absorption bands in the natural Brazilian amethyst specimen studied. These absorption bands were found to be anisotropic in nature. The shapes, the absorption coefficients, and the energy values at the peaks of the absorption curves depend on the orientation of the section under investigation as well as the orientation of the electric vector of incident radiation (Hassan and Cohen, 1974).

Green synthetic α-quartz doped with traces of Fe^{2+} ion exhibits a characteristic and complex absorption band in the near infrared related to the spin-allowed transition ($^5T_{2g} \rightarrow {}^5E_g$). Natural amethyst exhibits similar absorption in the same spectral region. For comparison, the absorption spectra of both natural amethyst and Fe^{2+} quartz are shown in Figures 1, 2, and 3 in the section orientations indicated. Details of spectra in the near infrared region are shown in inserts in the figures. These relatively thick samples were later reduced to the proper thicknesses necessary to show the details of the ultraviolet region, illustrated in the same figures. Most of the amethyst bands appear in the Fe^{2+} quartz absorption spectrum, except for the major band in the visible region (the θ band) shown in Figures 1–4 and 7–10. The absorption in the ultraviolet (α and β band region) is attributed by Cotton and Wilkinson (1966) to charge transfer transitions of trivalent iron compounds.

The complexity of absorption in this region is possibly due to the existence of Fe^{3+} in more than one environment in the α-quartz structure. While the α band appeared for all orientations of the synthetic Fe^{2+} quartz, the β band appeared only in plates cut from growth parallel to the positive rhombohedral face. The β band is resolved in natural amethyst (colored rhombohedral growth regions in natural α-quartz). The β band is thought to be related to Fe^{3+} in a specific environment available in the *r* growth regions.

The absorption spectra of Fe^{3+}-doped quartz as grown hydrothermally by Sawyer were measured in the orientations shown in Figure 4. The β band centered at 5.6 eV, which fails to appear in orientations parallel and perpendicular to the *c* axis, is very well developed in the orientation parallel to the positive rhombohedral face. This observation further indicates that the β band is structurally sensitive.

X-Irradiation Experiments

X-irradiation of sections of the natural amethyst cut perpendicular and parallel to the *c* axis had no effect on the absorbance within the spectral region studies. Thus the absorbing centers had reached saturation in the structure.

Upon X irradiating a Fe^{2+}-doped quartz section (A-84) cut both perpendicular and parallel to the *c* axis, the existing bands, except for κ_{complex}, are

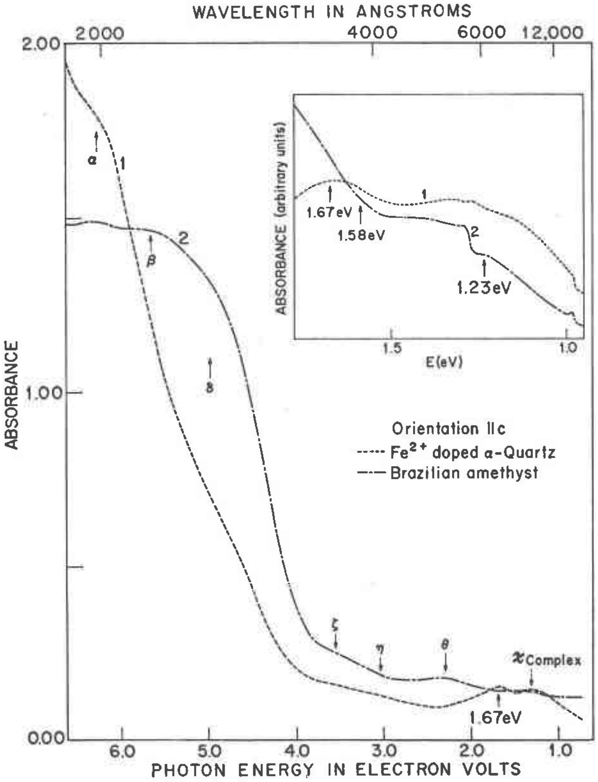

FIG. 1. Absorption spectrum for normal incidence of light on a section cut parallel to the *c* axis of synthetic α-quartz (A-84) doped with trace Fe^{2+} ion.

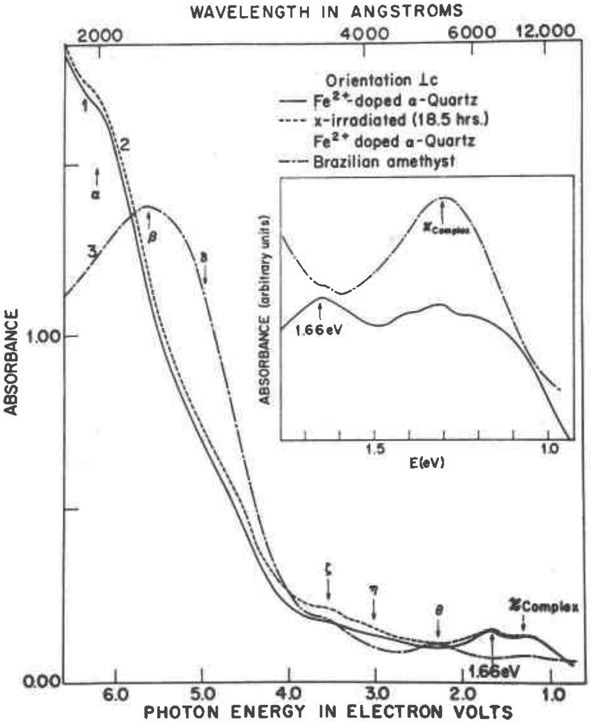

FIG. 2. Absorption spectra for normal incidence of light on a section cut perpendicular to the *c* axis of synthetic α-quartz (A-84) doped with trace Fe^{2+} ion before and after X irradiation.

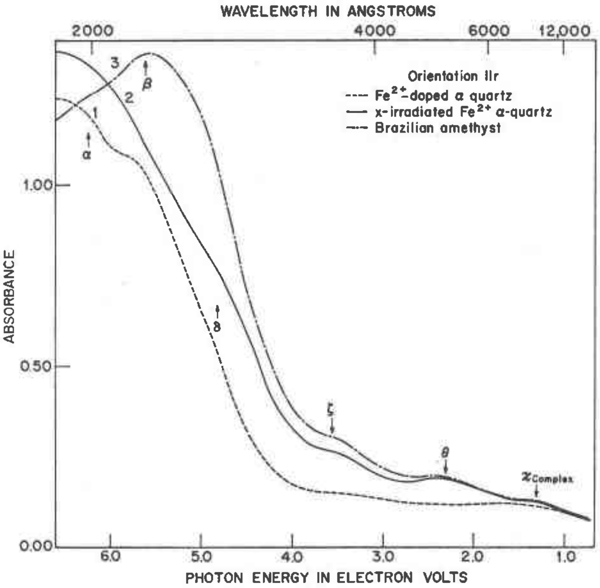

FIG. 3. Absorption spectra for normal incidence of light on a section cut parallel to a positive rhombohedral face of synthetic α-quartz (A-84) doped with trace Fe^{2+} ion before and after X irradiation.

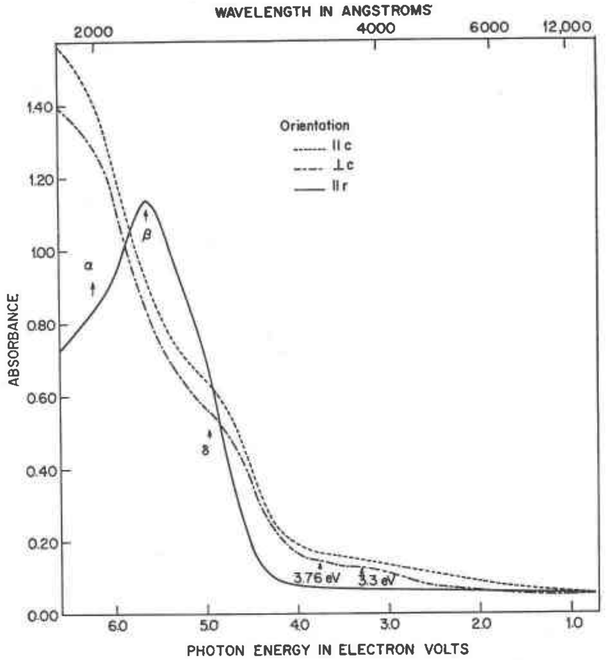

FIG. 4. The absorption spectra for normal incidence of light on differently oriented sections of Fe^{3+}-doped synthetic α-quartz (Y-5).

somewhat enhanced but no new bands develop. However, upon X raying a Fe^{2+}-doped quartz wafer cut parallel to a positive rhombohedral face, an amethyst color was produced. This amethyst color correlated with striations previously having the yellowish-brown color of the Fe^{3+} ion.

Upon X irradiation, a section cut perpendicular to the *c* axis of synthetic Fe^{3+} quartz (Y-5) acquired an amethystine color with a smoky tinge only below the rhombohedral faces, as sketched in Figure 5b. The color appeared to be both amethystine and smoky in the positive rhombohedral growth but only smoky in the negative rhombohedral growth. This further indicates that amethyst color precursors appear in positive rhombohedral growth while smoky color precursors are not specific but appear in both types of rhombohedral growth. The absorption spectra of both the uncolored and the amethyst-colored portions of the section are shown in Figure 5a as curves **2** and **3** respectively. The amethyst-colored parts of the specimen are refractively biaxial while the uncolored portions are uniaxial. For comparison the spectrum of natural amethyst in the same orientation is included (curve **4**).

X irradiation of a section cut parallel to the *c* axis of the Fe^{3+}-doped quartz crystal had little effect except to enhance the η band at about 3.02 eV and probably the ζ band at 3.54 eV. No amethyst color was seen in this orientation.

Upon exposure to X rays, a Fe^{3+}-containing α-quartz section cut parallel to a positive rhombohedral face acquired a homogeneous clear amethystine color. A decrease was observed in the optical density of the β band around 5.6 eV. Meanwhile the δ, ζ, and the θ bands in the visible region developed and continued to grow upon increasing the X-ray dose (Fig. 6). The existence of an isosbestic point (Fig. 7) indicates that the decrease in the Fe^{3+} absorption region in the ultraviolet is related to the increase of the bands on the longer wavelength side (Fig. 8).

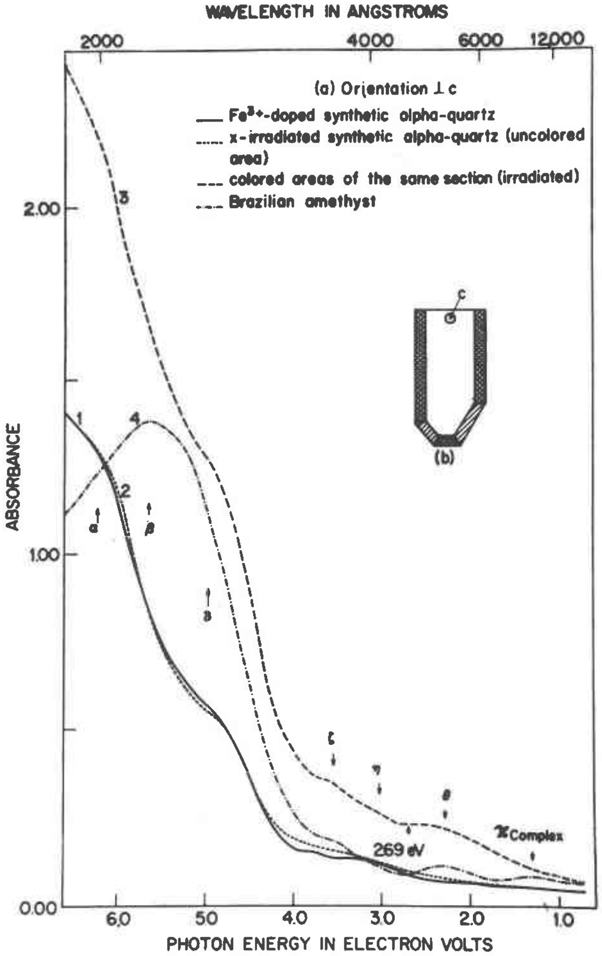

FIG. 5. (a) Absorption spectra for normal incidence of light on a section cut perpendicular to the *c* axis of Fe^{3+}-doped synthetic α-quartz (Y-5) before and after X irradiation; (b) the section investigated (inset).

Bleaching Experiments

The bands induced by X irradiation in Fe^{3+}-doped α-quartz (rhombohedral growth) cut parallel to a positive rhombohedral face can be bleached by light from a Hg,Xe lamp whose peak intensity falls at 2537 Å whereas the α and β bands in the ultraviolet region increased in intensity (Fig. 9). Heating produces a similar effect. Thus heating at 440°C for two hours was sufficient to return the crystal to the original optical state (Fig. 8).

The natural amethyst specimen studied (Fig. 10) behaved similarly. The fading characteristics of both synthetic and natural amethyst were almost identical (Hassan, 1970).

Regeneration of the Amethyst Color

Following thermal bleaching, the natural Brazilian specimen was recolored by irradiation with X rays at room temperature. A faint but clear amethystine color started developing in the first few minutes of irradiation and became deeper with further exposure (1.5 hours). The α and β bands (the ones that grow upon bleaching) faded upon X irradiation. The rate of growth of the ζ, η, θ, and the κ_{complex} bands were higher in the first 12 minutes of irradiation, then decreased gradually. However, the θ band continued to increase as depth of the amethyst color increased.

After the synthetic amethyst-colored Fe^{3+} quartz was thermally bleached, it was re-irradiated with X rays (Fig. 8) to produce an amethyst color with a smoky tinge. The general appearance of the growth characteristics was almost the same as the growth curves illustrating the process of coloration of the same specimen before thermal bleaching.

Heat Treatment of Synthetic α-Quartz

Heat treatment in air at 500°C for three hours of the Fe^{2+}-doped synthetic quartz section cut parallel to the c axis completely oxidized the Fe^{2+} to Fe^{3+}. This was evidenced by complete disappearance of the Fe^{2+} bands and growth of the Fe^{3+} bands in the ultraviolet region (Fig. 11). A yellow color appeared in the zones where the green color was located before oxidation. This observation strengthens the belief that the absorption band in the ultraviolet is mainly due to Fe^{3+} ions.

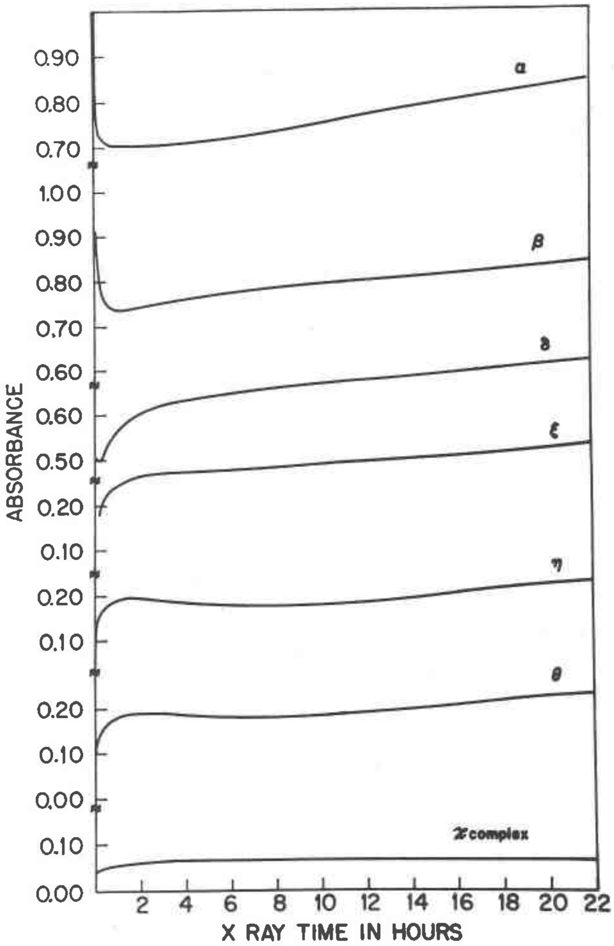

FIG. 6. The growth characteristics of the bands observed in a synthetic Fe^{3+}-doped α-quartz (H-95) section cut parallel to a positive rhombohedral face upon X irradiation.

In Fe^{2+}-doped quartz, the Fe^{2+} ion could have five possible environments (Cohen and Hassan, 1969). An interstitial Fe^{2+} ion situated near, and furnishing charge compensation for, two substitutional trivalent ions, is the most probable one because of the existence of voids and channels in the α-quartz structure that easily accommodate ions of comparatively large radii. The growth of the band in the ultraviolet region upon oxidation of the Fe^{2+} ion in α-quartz (Fig. 11) shows that this band is definitely related to Fe^{3+} ions which occupy the same sites as Fe^{2+} ions before oxidation. Since the Fe^{2+} ion is most likely interstitially incorporated, the band could thus be due to transitions related to interstitial Fe^{3+} ion. The appearance of the β band, before either X irradiation or heating, only in the Fe^{3+}-doped α-quartz section cut parallel to a positive rhombohedral face indicates that Fe^{3+} ion preferentially enters the α-quartz structure in the positive rhombohedral growth regions and mainly interstitially (in a distorted octahedral environment). The X-irradiation experiments indicate that only those Fe^{3+} ions in

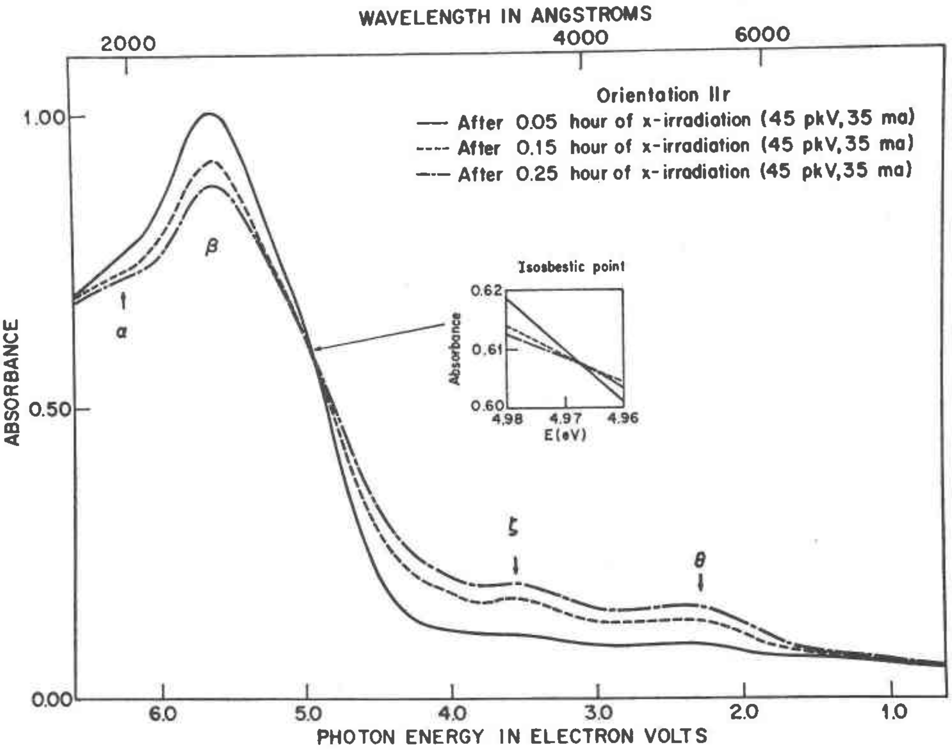

FIG. 7. Variation of the absorption spectrum with time of X irradiation of a section cut parallel to a positive rhombohedral face of synthetic α-quartz (H-95), doped with Fe^{3+} ions.

the positive rhombohedral sectors of growth are responsible for the amethyst color upon X irradiation.

Heating a wafer, cut parallel to a positive rhombohedral face from the synthetic Fe^{3+} quartz, at 500°C for two hours caused the production of a new phase in the form of small, brown microscopic particles. This indicates that some of the Fe^{3+} ions in the α-quartz are incorporated interstitially because substitutional Fe^{3+} ion would be impossible to precipitate under the described experimental conditions.

Discussion and Conclusions

The color of amethyst quartz is due to optical absorption bands induced by ionizing radiation. These induced optical bands developed only if impurity Fe^{3+} ion is present in a special environment in the α-quartz structure, usually in the positive rhombohedral growth regions. The presence of the Fe^{3+} ion in this particular site creates a specie of defect (or defects) which is the actual precursor of the color centers responsible for the amethyst color. Lehmann and Moore (1966b) correlated the intensity of a resonance line in the EPR spectrum of a natural amethyst with that of the optical absorption at 5450 Å (associated with the color), and found them to agree within ±15 percent. The calculated number of spins per unit volume was found to be equal to almost one third of the number of iron atoms present in the sample as determined by spectrographic analysis. Their observation is more easily understood if not all of the Fe^{3+} ions incorporated in the α-quartz are converted to the color center. Only one third of these ions, in the proper environment, are the actual precursors of the amethyst color centers.

The Fe^{3+} ion could have the following possible environments in the α-quartz.

1. Fe^{3+} substitutional for Si^{4+}, accompanied by an alkali ion or a proton for charge compensation.
2. Fe^{3+} interstitial, furnishing charge compensation for substitutional cations having lower valency than Si^{4+}.

Barry and co-workers (1964, 1965) believe that the defect precursor center is a Fe^{3+} substitutional for Si^{4+} with charge neutralization achieved by an alkali ion (S_1 centers). Lehman and Moore (1966b) described a center (*I*) which they identified as an interstitial Fe^{3+}. Matarrese, Wells, and Peterson

(1966) assigned the (I) centers to a substitutional site. S_1 centers were found to be dominant in citrine with no amethyst color (Lehmann and Moore, 1966a). X or γ irradiation of quartz containing iron produces the amethyst color without trace of the S_1 spectrum (Lehmann and Moore, 1966a). Another spectrum was found and labelled S_2 (substitutional Fe^{3+} with a proton as a charge compensator), but this is not the color center directly responsible for the amethyst color (Matarrese, Wells, and Peterson,1966). A fourth spectrum has been identified and described by Lehmann and Moore (1966b) that presumably is due to the color center which they identify as Fe^{4+}.

The experimental findings of the present investigation indicate that the Fe^{3+} ion located in the positive rhombohedral growth sectors produces the β absorption band in the ultraviolet and is the amethyst color precursor. Upon X irradiation, the amethyst color center develops only if the band exists before irradiation. This ligand-cation charge transfer band is assigned an interstitial rather than a substutional site for the Fe^{3+} ion (Table 2), since it grows upon oxidation of Fe^{2+} ions in Fe^{2+}-doped α-quartz. Therefore, the present data are believed to be more consistent with an interstitial Fe^{3+} as the main precursor for the amethyst color. However, a substitutional Fe^{3+} is another possible precursor for another existing color center, but it is not always related to the amethyst color, as will be explained.

More evidence for the interstitial site of Fe^{3+} is gained from the bleaching experiments. Optical and thermal bleaching experiments in this work almost restored the β band to its original intensity as measured before irradiation. Thermal bleaching experiments in amethyst done by Lehmann and Moore (1966b) caused an increase in I centers (interstitial Fe^{3+}). In this work, however, heating the specimens at a temperature higher than 440°C (500°C) for two hours resulted in the permanent disappearance

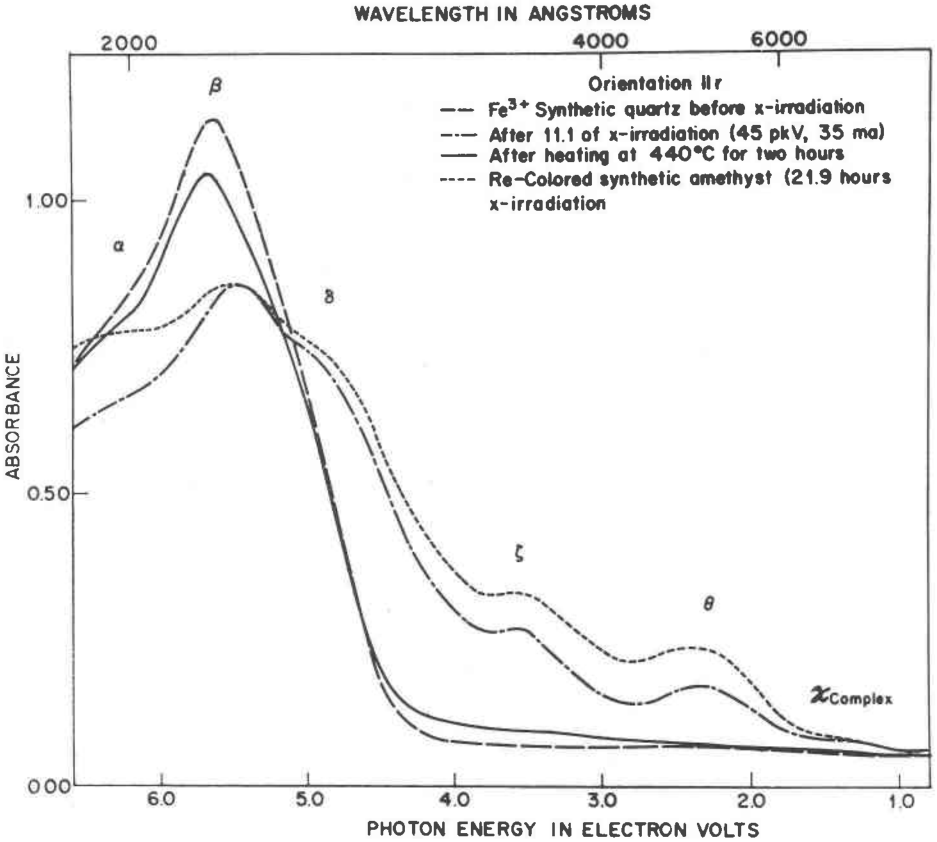

FIG. 8. Absorption spectra for normal incidence of light on a section of synthetic Fe^{3+}-doped α-quartz (H-95) cut parallel to positive rhombohedral face before and after X irradiation, after thermal bleaching and after recoloration.

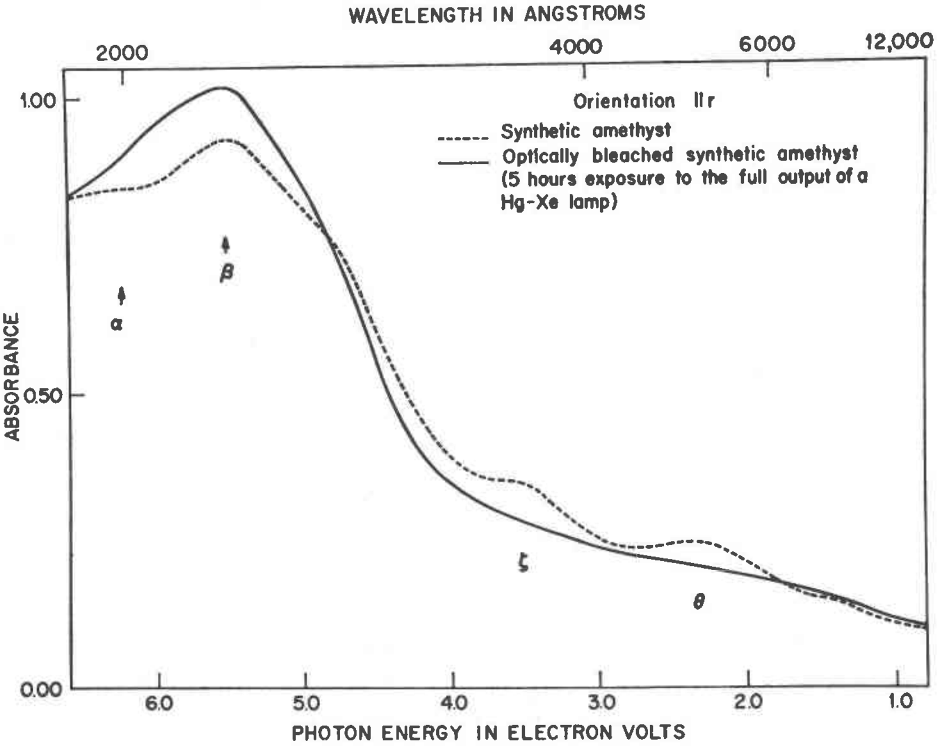

FIG. 9. Absorption spectra for normal incidence of light on a section of synthetic amethyst (H-95) before and after optical bleaching.

of the amethyst color in the specimens investigated, even after X irradiation, and the sections became nearly uniaxial. Heat treatment experiments done by Barry and Moore (1964) and also by Barry, McNamara, and Moore (1965) resulted in similar findings and permanently destroyed the centers responsible for the biaxiality and pleochroism in amethyst even after X irradiation. They attributed this to the equal redistribution of the substitutional Fe^{3+} upon heating at 600°C and 650°C. This redistribution of Fe^{3+} in the sites substitutional for Si^{4+} is considered to be very improbable because of the partially covalent nature of the Si–O bond.

The heat treatment results described in the same paper are better understood if assigned an interstitial site for the Fe^{3+} in a restricted environment. Interstitial Fe^{3+} is further indicated from the heat treatment experiments which indicate the precipitation of a new phase. No experiments were done to identify this new phase, which is likely an Fe^{3+}-containing phase. Lehmann and Moore (1966b) identified a line in their EPR spectrum due to Fe^{3+} oxide in synthetic amethyst. A similar line was found in natural amethyst by Matarrese, Wells, and Peterson (1966), who suggested electrolysis experiments to move the Fe^{3+} about in the structure at elevated temperatures. The diffusion experiments done by Hassan (1970) resulted in the permanent disappearance of the amethyst color after X irradiation, adding evidence to the idea that those Fe^{3+} ions directly related to the amethyst color are mainly in interstitial sites. It seems that these interstitial sites are restricted to a given environment if the amethyst color is to be produced. Once the interstitial Fe^{3+} is forced to move away from this region, by heating or by electrolysis, such environment is destroyed and the color will not be regenerated even upon irradiation. A proposed interstitial site (I_r) which conforms to the experimental findings in this work (taking in consideration the size of the channels and the ion size of Fe^{3+}) is the void which lies at the intersection of the channel perpendicular to the positive rhombohedral face and that which lies at 45° from the c axis (Hassan, 1970).

It seems that the substitutional Fe^{3+}, although not directly related to the color, is present in most of the amethyst studied, as evidenced by optical absorption and EPR techniques. It is tempting to consider a model where an interstitial Fe^{3+} is near a substitutional one. The present information can be summarized as follows:

$$(Fe^{3+})_{Sub.} \underset{390^{\circ}C}{\overset{X\ rays}{\rightleftharpoons}} (Fe^{3+})_{Sub.} + hole$$

(α band) (θ band)

$$(Fe^{3+})_{Int.} \underset{390^{\circ}C}{\overset{X\ rays}{\rightleftharpoons}} (Fe^{3+})_{Int.} + electron$$

(β band) ($\kappa_{complex}$ band)

Combining these, we therefore have:

$$(Fe^{3+})_{Sub.} + (Fe^{3+})_{Int.}$$

$$\underset{390^{\circ}C}{\overset{X\ rays}{\rightleftharpoons}} (Fe^{3+}{}_{Sub.} + hole) + (Fe^{3+}{}_{Int.} + electron)$$

$\alpha + \beta$ bands $\theta + \kappa_{complex}$ bands

The existence of both the θ and $\kappa_{complex}$ bands is necessary if the amethyst color is to be produced. The color centers responsible for the amethyst color are believed to be a mixture of both of the above centers, an electron trapped on an interstitial Fe^{3+}, and a hole trapped on a substitutional Fe^{3+}. Table 2 summarizes the possible nature of the bands involved in the proposed model. The possibility of the involvement of substitutional Al^{3+} in the color production needs investigation. We can consider the idea that

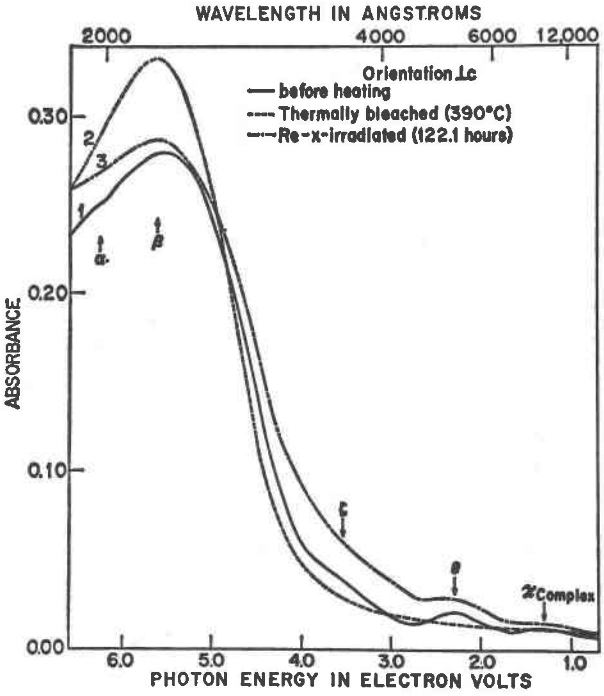

FIG. 10. Absorption spectra for normal incidence of light on a section of Brazilian amethyst (R-1454) before heating, after heating at 390°C for two hours, and after irradiation with X rays.

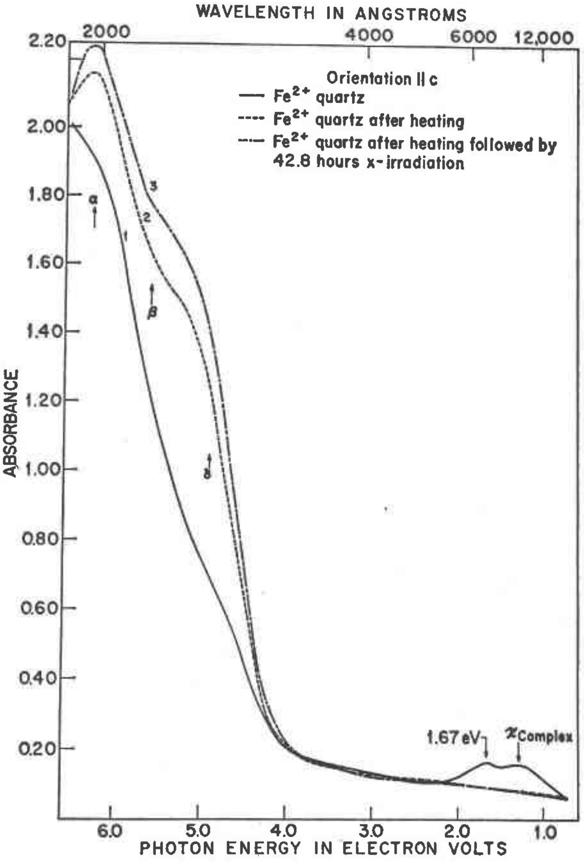

FIG. 11. Absorption spectra for normal incidence of light on a section of Fe^{2+} quartz (A-84) cut parallel to the c axis after heating at 500°C for three hours, and after heating followed by 42.8 hours of X irradiation.

TABLE 2. Properties of the Optical Bands in Natural and Synthetic Amethyst Quartz

Band designation	Probable nature of center	Remarks
α	Fe^{3+} substitutional for Si^{4+} (tetrahedral coordination).	Appears in amethyst, Fe^{3+} and Fe^{2+} doped α-quartz.
β	Interstitial Fe^{3+}, precursor of the amethyst color center. (distorted octahedral environment).	Grows upon oxidation of Fe^{2+}; Intensity decreases with growth of color centers and increases on fading of color centers.
θ	Substitutional Fe^{3+} + hole, with the electron trapped on an interstitial Fe^{3+}.	Directly related to the amethyst color, grows upon fading of the β band.
$\kappa_{complex}$	Fe^{2+} interstitial (distorted octahedral environment).	Associated with the amethyst color, grows upon fading of the β band.

some of the interstitial Fe^{3+} ions trap electrons furnishing the charge compensation for a substitutional Al^{3+}. After the interstitial Fe^{3+} ions diffuse away (by heating of the amethyst sections at 400° − 500°C, or by electrolysis), irradiation of both substitutional Al^{3+} and Fe^{3+} would trap holes, but the electrons in this case would be trapped on a nearby alkali (or a proton). This results in both the well-known Al^{3+} center responsible for the smoky color observed in some of the present experiments and in the S_1 and S_2 centers, described by Barry and co-workers (1964, 1965) and by Lehmann and Moore (1966a), found to exist in all Fe^{3+} containing α-quartz (amethyst, bleached amethyst, and citrine).

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