

## Amethyst color in quartz, the result of radiation protection involving iron

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### Abstract

Interstitial  $\text{Fe}^{3+}$  impurity in the growth-loci of the terminal major rhombohedral faces of quartz protects these regions from becoming smoky-colored if the iron content is in large excess of the  $\text{Al}^{3+}$  impurity content. The latter is responsible for the trapped-hole centers causing the smoky color, in the presence of ionizing radiation. Growth-loci of terminal minor rhombohedral faces may become smoky even though large excess of substitutional  $\text{Fe}^{3+}$  compared to  $\text{Al}^{3+}$  impurity, is present.

The oxidation of interstitial  $\text{Fe}^{3+}$  to  $\text{Fe}^{4+}$  furnishes an electron for quenching the trapped-hole centers on oxygens adjoining substitutional  $\text{Al}^{3+}$  sites as they are formed thus preventing the appearance of smoky color. The resulting amethyst color is due to an absorption band related to the  $\text{Fe}^{4+}$  produced.

Since  $\text{Fe}^{3+}$  only predominates over  $\text{Fe}^{2+}$  in natural quartz formed under shallow-growth conditions, usually in cavities or geodes, amethyst color in quartz is limited to these sources.

### Introduction

Iron may be present in quartz in three valence states,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$ . All three states may be present in interstitial sites, only  $\text{Fe}^{3+}$  being in a substitutional  $\text{Si}^{4+}$  site.

Ferrous iron predominates in quartz produced under non-surface conditions as in deep-seated pegmatites while ferric iron tends to be present in quartz growth under near-surface conditions as in geodes, amygdaloidal cavities or hydrothermal veins. Amethyst quartz is limited to these latter types of localities while smoky quartz can be found that has grown under both deep-seated and surface conditions.

In the majority of cases, the amethyst color is limited in nature to crystals exhibiting twinning on the Brazil Law in the growth-loci of terminal major rhombohedral, *r* faces (Fron del, 1962, p. 171-173). The growth-loci of minor rhombohedral untwinned faces rarely exhibit amethystine color in natural amethyst but can be smoky, or orange if substitutional  $\text{Fe}^{3+}$  is present in the crystal that exhibits amethystine color in the *r*-growth regions. Commonly the *z*-growth regions are colorless, and Brazil twinning is always absent.

### Previous work

Recently, Cohen and Makar (1985) found that the  $\text{Ti}^{3+}$ -related rose color in a single crystal of rose quartz was also limited to the growth loci of the terminal major rhombohedral faces. Massive rose quartz commonly grows on *r* and incorporates large amounts of substitutional alu-

minum impurity (see Table 1 for analyses) compared to the titanium and ferrous contents, Cohen and Makar (1984). It was found that presence of interstitial  $\text{Fe}^{2+}$  and  $\text{Ti}^{3+}$  offered radiation protection against formation of the Al trapped-hole centers in a single crystal where the ratio of  $(\text{Fe} + \text{Ti})/\text{Al}$  is 0.13, but radiation protection is absent in massive rose quartzes where the ratio ranges to 0.016. There is no twinning related to the rose-colored zones, however rutile is always present in the massive material, often microscopic in size.

Halperin and Ralph (1963) found that room temperature X-irradiated Bell Labs Synthetic quartz R-27 (see table 1 for analytical data) cooled to 77°K contained new absorption bands at ~2.30 eV and 4.35 eV in the  $\pi$  polarized spectra ( $\pi$  = electric vector parallel to the optic axis, *c*) as shown in Figure 1. The band peak at ~2.30 eV is in the region of the band peak related to  $\text{Fe}^{4+}$ . Cohen (1984) found the band peak for  $\text{Fe}^{4+}$  in  $\pi$  at 2.27 eV as well as in  $\sigma$  ( $\sigma$  = electric vector perpendicular to the optic axis, *c*, therefore in the *a* plane) in a specimen oriented parallel to the *c*-axis, in (1100). In a specimen oriented perpendicular to *c* (0001), the peak maximum in  $\sigma_{\parallel a}$  is 2.30 eV and in  $\sigma_{\perp a}$  is at 2.26 eV; the optical band being dichroic in the *a* plane.

Cox (1977) reported three different biaxial bands related to  $\text{Fe}^{4+}$ . However, he gave no chemical analysis for the natural amethyst studied. Cox also presented data that he interpreted as evidence that the  $\text{Fe}^{4+}$  is substitutional in the same paper and in an earlier one (Cox 1976) concerning an EPR study of the same amethyst quartz material.

Table 1. Emission analyses of rhombohedral growth in smoky and rose quartz in atoms per  $10^6$  Si atoms\*

Element	Synthetic (Smoky) Quartz** Bell Labs R-27 (plasma method)	Rose Quartz Massive, Brazil	Rose Quartz Single Crystal, Sapucia Brazil, NMNH 115272
Al	743	2230	112
Fe	27	11	11
Ge	600	-	-
Ti	< 13	25	4
Li	729	1740	260
Na	< 26	52	210
<b>Ratio:</b>			
Fe/Al	0.036	0.0049	0.098
(Fe + Ti)/Al	0.054	0.016	0.13
Al/(Li + Na)	1.02***	1.20	0.24

\*from D. Partlow, (1984). PhD Thesis, University of Pittsburgh, in progress.  
 \*\*major Rhombohedral growth suggested (see text).  
 \*\*\*excluding Na content.

## Discussion

### *Quartz with iron impurity in excess of aluminum impurity in major rhombohedral growth*

The specimen discussed here, Sample No R-1454 from the National Museum of Natural History has been described in an earlier paper (Hassan and Cohen, 1974) along with a detailed spectrophotometric study. Its absorption spectrum is shown in Figure 2. The oscillator strength of  $Fe^{4+}$  in the same specimen has recently been determined (Cohen, 1984).

An analysis by atomic absorption for aluminum and iron in major and minor rhombohedral growth is given in Table 2(a) and the ratio of impurities of major to minor rhombohedral growth by emission analysis is given in Table 2(b). It is seen that the ratio of Fe/Al is 4.94 for major rhombohedral growth and 5.75 for minor rhombohedral growth. The major rhombohedral growth exhibits Brazil twinning and there is uniform amethyst color in both the *d*- and *l*-alternating optical twins in the crystal investigated. The untwinned minor rhombohedral growth exhibits only a variable intensity of wispy smoky color. These observations were made in a thick section (> 1 cm) cut perpendicular to the optic axis.

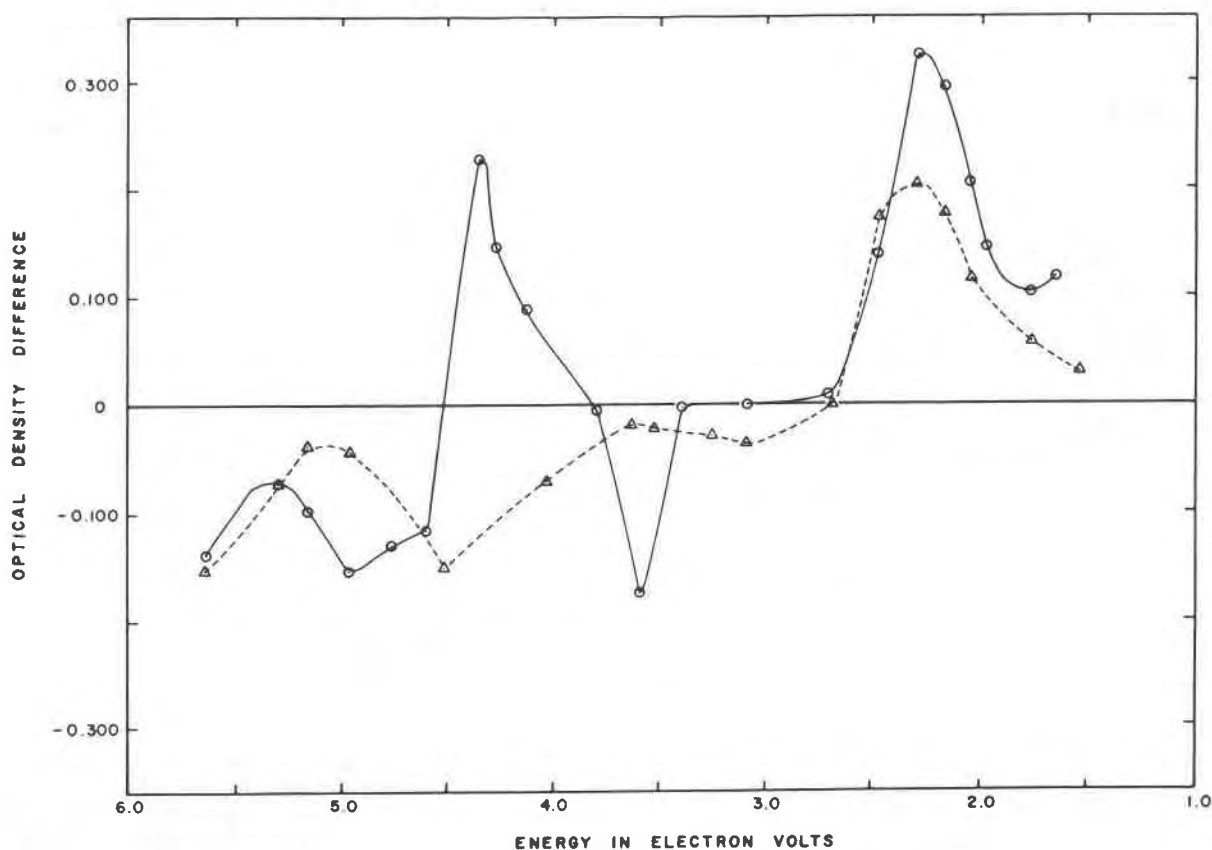


Fig. 1. —  $\pi$  spectrum, difference between 295°K and 77°K after X-irradiation of sample R-27; ---- same for  $\sigma$  spectrum.

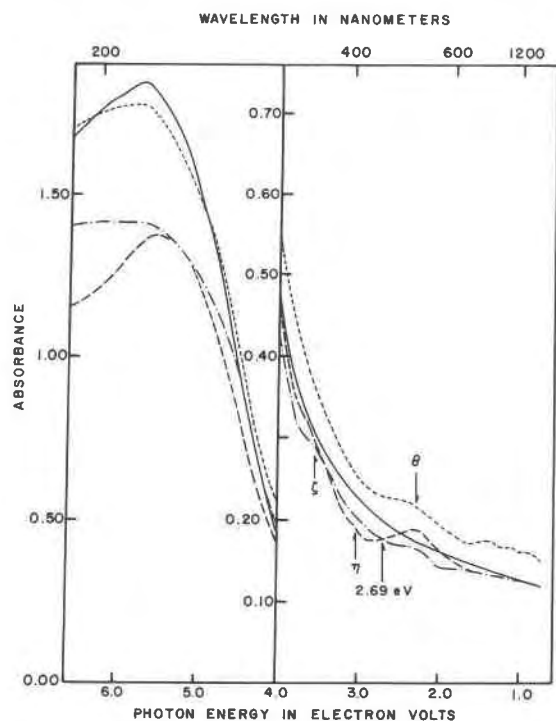


Fig. 2. Absorption Spectra of Brazilian Amethyst, R-1454 cut perpendicular to *c*-axis: --- natural spectrum, — after heating at 500°C, - · - · X-rayed 6 min., - - - X-rayed 18.5 hrs.

Diffusion of  $\text{Na}^+$  under influence of an electric field along *c*-channels of a plate cut from major rhombohedral growth of this crystal caused the amethyst color to disappear and upon reirradiation with X-rays a smoky color took its place. This is evidence that the iron in the  $\text{Fe}^{4+}$  valence state is interstitial and diffuses out of the crystal under an electric field to be replaced by  $\text{Na}^+$  from a Na-amalgam anode (Hassan, and Cohen, 1974). After removal of interstitial iron there is no radiation protection offered against the formation of the Al trapped-hole color centers which then appear just as in minor rhombohedral growth. The substitutional  $\text{Fe}^{3+}$  present requires charge compensation from interstitial impurities. Upon treatment with ionizing radiation if this iron were to be oxidized to  $\text{Fe}^{4+}$  it would furnish an electron to the interstitial charge compensator ( $\text{Na}^+$ ,  $\text{Li}^+$  or  $\text{H}^+$ ) which would then have to carry the electron to the Al trapped-hole center formed, to quench it. If this were the case one would have amethyst color in both major and minor rhombohedral growth. It would not explain replacement of amethyst color by smoky color in the diffusion experiment as substitutional  $\text{Fe}^{3+}$  is fixed and cannot be removed without breaking several tetrahedral covalent Fe-O bonds, while interstitial  $\text{Fe}^{4+}$  is much more mobile being located in open channels and can be replaced easily by other cations under an electric field at elevated temperature.

The fact that synthetic amethyst cannot be produced unless aluminum impurity is present in addition to iron in

Table 2. Analyses of natural amethyst rhombohedral growth, specimen NMNH No. R-1454

(a) by atomic absorption, in atoms per $10^6\text{Si}$ atoms*				
Element	Major Rhombohedral growth, R	Minor Rhombohedral growth, z	Difference (r-z)	Ratio r/z
Al	$18 \pm 1$	$12 \pm 1$	6	1.5
Fe	$89 \pm 3$	$69 \pm 2$	20	1.3
Ratio Fe/Al	4.94	5.75		
Ratio Fe(r-z)/Al(r)				1.11
Ratio Fe(r-z)/Al(z)				1.67

(b) by emission analysis, ratio of major rhombohedral growth to minor rhombohedral growth	
Element	Ratio r/z
Al	2.6
Fe	1.4
Mn	1.4
Ge	0.58
Ba	1.6
Ni	3.8
Ti	2.7
Zr	2

\*from Cohen (1984)

major rhombohedral growth (Sawyer, pers. comm., 1964) is additional evidence that the  $\text{Fe}^{4+}$  is produced as a result of oxidation of  $\text{Fe}^{3+}$  to  $\text{Fe}^{4+}$  upon treatment with ionizing radiation in order to furnish an electron to quench, or prevent, the growth of the aluminum trapped-hole center.

In addition to amethyst specimens that contain no smoky quartz centers (Cohen, 1956), it is not uncommon for amethyst to contain the aluminum trapped-hole centers. The amethyst studied here, Specimen R-1454 exhibits the  $A_3$  center at 3.05 eV, referred to as the  $\eta$  center in Figure 2, taken from the Ph.D. thesis of F. Hassan, (1970). The  $A_3$  center was not discovered by Nassau and Prescott until 1975, so the absorption band was not connected to

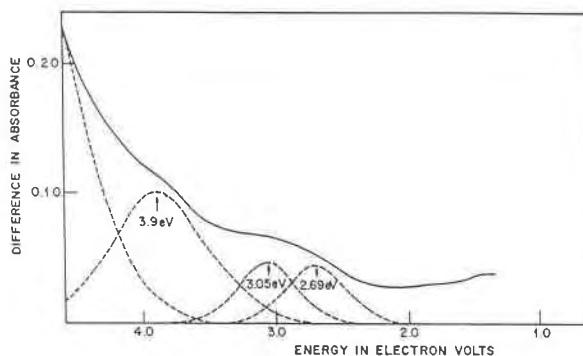


Fig. 3. Absorption spectral difference between natural spectrum and spectrum after 18.5 hr. X-ray in Figure 2. The spectrum is that of smoky quartz with 3.9 eV = B band, 3.05 eV =  $A_3$  band and 2.69 eV =  $A_2$  band.

this center until their work was published. The protection against formation of the Al trapped-hole centers is related to the dispersion of the  $\text{Fe}^{3+}$  in the structure.

Figure 3 shows the effect of heat bleaching the R-1454 sample at  $500^\circ\text{C}$  and then X-raying until there is no further change in the absorption spectrum (18.5 hours at 45 pKV and 35 ma, 5.4 cm from the Be window of a Machlett AEG-50-T X-ray tube with tungsten target, (Hassan, 1970). The difference between the amethyst spectrum in the untreated natural specimen and after the X-irradiation of the heat bleached stage indicates that the only growth other than return of the original spectrum is appearance of the B trapped-electron center and the  $\text{A}_3$  and  $\text{A}_2$  Al trapped-hole centers.

It is of interest that treatment with ionizing radiation in the laboratory produces more intense Al trapped-hole centers than appear in nature. The same phenomenon occurs in massive rose quartz which turns smoky with ionizing radiation in the laboratory, but is not known by the author to be found in nature. The natural radioactivity to which these quartzes are subject may have a different effect than the usual X-ray or  $^{60}\text{Co}$  radiation but more likely is the possibility of thermal bleaching in nature, the  $\text{Fe}^{4+}$  and  $\text{Ti}^{3+}$  centers being more thermally stable than the Al centers.

Balitsky (1977) has avoided the need to control the aluminum content and thus production of possibly smoky color by growing synthetic amethyst in the absence of alkali using  $\text{NH}_4\text{F}$  solutions so that the room temperature metastable H-Al centers form instead of the stable alkali-Al centers. Balitsky (1980) points out that deeply-colored amethyst quartz requires the presence of alkali ions thus the presence of incipient Al-alkali centers are necessary for  $\text{Fe}^{4+}$  to form upon treatment with ionizing radiation. A large excess of iron over aluminum is probably necessary to preclude formation of the smoky centers due to the fact that the former can be present as both interstitial  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  as well as substitutional  $\text{Fe}^{3+}$  and only the interstitial  $\text{Fe}^{3+}$  can furnish electrons to quench the Al trapped-hole centers.

#### *Quartz with aluminum impurity in excess of iron impurity in rhombohedral growth<sup>1</sup>*

In this section a rhombohedral growth synthetic quartz crystal having excess aluminum impurity over iron impurity will be discussed. This is specimen R-27 grown at Bell Laboratories. A recent analysis is given in Table 1. An earlier less precise analysis (Cohen and Smith, 1958) differed mainly in reporting a fourfold greater iron content. It is seen that the Fe/Al ratio is 0.036. This compared to the ratio in major rhombohedral growth in amethyst, in Table 2, 4.94, is very low. It is presumed that the iron in this

synthetic quartz will mainly be in the ferric state before X-ray treatment.

Halperin and Ralph (1963) X-rayed this crystal at room temperature and ran the polarized spectra in a specimen cut parallel to the c-axis, then cooled the specimen and ran the polarized spectra again at liquid nitrogen temperature. Upon taking the difference spectrum in  $\pi$  between the room temperature spectrum and the  $77^\circ\text{K}$  spectrum they found that absorption bands appeared with peaks at  $\sim 2.30$  eV and 4.35 eV.

In this work their difference spectra have been replotted using the data given in their Figure 4, shown in Figure 1 in this paper. In addition to appearance of these two bands at  $\sim 2.30$  eV and 4.35 eV, minima in the absorption coefficients occur in the  $\pi$  spectrum at 3.60 eV and 4.96 eV and in the  $\sigma$  spectrum at 3.1 eV and 4.53 eV.

In replotting it was found that the 2.30 eV peak occurred in both  $\pi$  and  $\sigma$  spectra at this same energy. In the  $\pi$  spectrum of the wafer, 0.097 cm thick, an absorption coefficient of  $3.34\text{ cm}^{-1}$  was found and  $W_{1/2}$  (width of band at half-maximum) was 0.44 eV. For the  $\sigma$  spectrum the absorption coefficient was  $2.11\text{ cm}^{-1}$  with a  $W_{1/2}$  of 0.56 eV. Using the equation of Dexter (1956) and the oscillator strength for  $\text{Fe}^{4+}$  calculated by Cohen (1984) as  $0.011 \times 2.3 (= 0.025)$ , one calculates  $2.1 \times 10^{18}$   $\text{Fe}^{4+}$  ions per  $\text{cm}^3$  for the 2.30 eV band in  $\pi$  and  $1.6 \times 10^{18}$  in  $\sigma$ . This is 73 and 60  $\text{Fe}^{4+}$  ions per  $10^6$  Si respectively. If one compares these values to the analysis for iron in R-27 in Table 1, it is seen there is agreement within the precision of emission analysis with the value of 27 Fe ions per  $10^6$  Si. One can conclude from this result that the 2.30 eV band is indeed the  $\text{Fe}^{4+}$  absorption band and that apparently all the iron in the sample was interstitial  $\text{Fe}^{3+}$  before the sample was cooled. A minimum at 3.1 eV in the  $\sigma$  spectra is related to decrease in absorption of the  $\text{A}_3$  band in smoky quartz. Nassau and Prescott (1978) give a peak in minor rhombohedral growth at 2.95–3.1 eV in  $\sigma$  for the  $\text{A}_3$  band.

The lattice constants of specimen R-27 determined by Cohen and Sumner (1958) are  $a = 4.9139$  and  $c = 5.4052\text{Å}$  with  $D$  calc = 2.6483. These authors conclude that this specimen contains both substitutional and interstitial impurities, based on these lattice constants. This is confirmed by the high substitutional germanium and aluminum contents shown in Table 1. The Li and Na must be interstitial and it is considered based on the number of  $\text{Fe}^{4+}$  color centers that all the iron is interstitial. The titanium is probably divided between interstitial and substitutional sites. The large cell constants for this quartz specimen compared to a specimen with very low impurity content,  $a = 4.9129$  and  $c = 5.4045\text{Å}$  would indicate that the voids in sample R-27 are larger than in pure quartz and may allow ample room for an interstitial  $\text{Fe}^{4+}$  to be near a trapped-hole. Then, the very high substitutional  $\text{Ge}^{4+}$  content as shown in Table 1 is unusual even among Ge-doped synthetic quartzes and is almost three orders of magnitude larger than found in most natural quartz.

It is concluded that Al trapped-hole centers in Specimen R-27 are not stable at  $77^\circ\text{K}$  when interstitial  $\text{Fe}^{3+}$  is pres-

<sup>1</sup> Records concerning orientation of seed producing the synthetic crystals discussed in this section are not available. The appearance of the  $\text{Fe}^{4+}$  band suggests major rather than minor rhombohedral growth.

ent; the  $\text{Fe}^{3+}$  furnishing an electron to quench the Al trapped-hole center, being oxidized to  $\text{Fe}^{4+}$ .

#### *Interstitial $\text{Fe}^{4+}$ versus substitutional $\text{Fe}^{4+}$ in major rhombohedral growth*

It has long been considered, by several investigators, that  $\text{Fe}^{4+}$  in amethyst quartz is in a substitutional  $\text{Si}^{4+}$  site of  $C_2$  symmetry, and is produced from  $\text{Fe}^{3+}$ , occupying this site, by ionizing radiation (Barry et al. (1965), Barry and Moore (1964), Lehmann and Moore (1966), Lehmann (1967) (1975), Cox (1976) (1977)). It is also known that  $\text{Fe}^{3+}$  can occur interstitially in quartz where it could also be in a site of  $C_2$  symmetry, Cohen and Hassan (1970). The 538.5 nm (2.30 eV) band of Cox is the 2.27–2.30 eV band related to  $\text{Fe}^{4+}$ . The 527 nm (2.35 eV) band of Cox is most likely the gaussian band of  $\text{Ti}^{3+}$  and the 599.5 nm (2.068 eV) band of Cox is without doubt the  $A_1$  band of an aluminum trapped hole center in a region not afforded radiation protection by interstitial  $\text{Fe}^{3+}$ . It is exceedingly unlikely that  $\text{Fe}^{4+}$  could exhibit two biaxial bands that were not found by careful earlier work on the anisotropy of amethyst. These different assignments of the 527 nm and 599.5 nm bands if correct make Cox's energy levels of  $\text{Fe}^{4+}$  invalid. It is unfortunate that he did not obtain synthetic amethyst material with a lower level of impurity considering his otherwise excellent insight into the amethyst problem.

Scala and Hutton (1976) consider the  $\text{Fe}^{3+}$  in the I center of  $\alpha$ -quartz to be substitutional for silicon however they reach no conclusions concerning the  $\text{Fe}^{3+}$  in the  $S_1$  center site location, namely whether it is substitutional or interstitial.

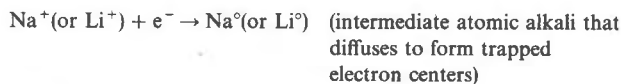
Barry et al. (1965) attribute unequal  $\text{Fe}^{3+}$  population to unequal distribution in the three silicon sites during crystal growth. Nassau and Prescott (1978) have shown unequal distribution of aluminum in minor rhombohedral growth. They found that growth anisotropy for Al was less in major rhombohedral regions.

If  $\text{Fe}^{3+}$  when interstitial offers charge compensation for  $\text{Al}^{3+}$  then it might be expected to have similar biaxial anisotropy. This Al trapped-hole biaxial anisotropy is called "differing non-uniaxial pleochroism produced by irradiation, reflecting a growth-induced anisotropy in hydrothermal quartz" by Nassau and Prescott (1978). This anisotropy for the  $\text{Fe}^{4+}$  band peak in the basal plane of specimen R-1454 is  $\sigma_{\parallel a} = 0.808 \text{ cm}^{-1}$  divided by  $\sigma_{\perp a} = 0.485 \text{ cm}^{-1}$  (Cohen, 1984) giving an anisotropy ratio of 1.67. The number of  $\text{Fe}^{4+}$  ions in  $\sigma_{\parallel a} = 7.3 \times 10^{17}$  per  $\text{cm}^3$  and in  $\sigma_{\perp a} = 4.3 \times 10^{17}$  per  $\text{cm}^3$  giving a ratio of 1.70 based on an oscillator strength of 0.025. This is close to the value using the absorption coefficient ratio of peak heights directly. This compares with a dichroic ratio of  $\sigma_{\text{max}}/\sigma_{\text{min}}$  in the basal plane at 2.5 eV in smoky quartz of 1.37, mostly  $A_2$  and  $A_3$  band absorption (Nassau and Prescott, 1978). The charge-transfer character of the  $\text{Fe}^{4+}$  band at 2.25–2.3 eV based on its oscillator strength of 0.025 is not inconsistent with a model, for the center responsible for this band, of a hole trapped between a substitutional-interstitial pair of  $\text{Fe}^{3+}$  ions. This is the C center suggested by Lehmann

and Moore (1966). However, the calculation of the number of  $\text{Fe}^{4+}$  producing the 2.30 eV band in sample R-27 is essentially all the iron present according to the analysis given in Table 1. This would rule against this model. With this in mind one might suggest charge transfer between the oxygen, adjoining the aluminum, on which the hole was formerly trapped and an interstitial  $\text{Fe}^{4+}$ . This  $\text{Fe}^{4+}$  could be at a  $C_2$  site. The coordination number of the interstitial site would be determined by the surroundings of the interstitial  $\text{Fe}^{4+}$ . If it offers charge compensation for an  $\text{Al}^{3+}$  ion it could be located near a center responsible for either the  $A_1$ ,  $A_2$  or  $A_3$  optical band. The  $A_3$  band is caused by the well known Al trapped-hole center namely a hole trapped on an oxygen adjoining an aluminum as shown by Nassau and Prescott (1975). Cohen and Makar (1982) suggest that the  $A_2$  band is related to an Al center with a trapped hole on an oxygen with another non-bonded oxygen on the tetrahedron and the  $A_1$  band is related to an Al center with a trapped hole on an oxygen with two more non-bonded oxygens on the tetrahedron. Thus the  $A_3$  center would be bound to the quartz lattice by three oxygens, the  $A_2$  center by two oxygens and the  $A_1$  center by only one oxygen. This would allow considerable variation around the interstitial  $\text{Fe}^{4+}$  depending on whether it was near an  $A_1$ ,  $A_2$  or  $A_3$  incipient center or combinations of them.

### Conclusions

Determination of the mechanism for the formation of the  $\text{Fe}^{4+}$  in  $\alpha$ -quartz has led to new insight concerning its general location in this structure. The formation of  $\text{Fe}^{4+}$  requires the presence of incipient Al trapped-hole centers and it is formed as a result of simultaneous quenching of these trapped-holes when the quartz is subjected to ionizing radiation in nature or in the laboratory as follows:



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