Biaxial Color Centers in Amethyst Quartz

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Abstract

Anisotropy of the characteristic absorption bands in a natural amethyst crystal from Brazil is demonstrated by the dependence of the value of the absorption coefficient upon the direction of the electric vector of incident light within the 4.13-0.95 eV region, for differently oriented sections of the crystal. The absorption indicatrix is used for interpreting the observed optical absorptions. A new absorption band in the 6.20 eV region is reported. A complex absorption band in the 5.60 eV region, usually attributed to a transition related to ligand-cation charge transfer in Fe" ions, is clearly resolved into at least three bands.

The biaxiality and pleochroism of amethyst is explained as due to the existence of strongly anisotropic color centers, related to iron, of orthorhombic or lower symmetry. Upon bleaching the amethyst color, either optically or thermally, the biaxiality disappears. This anomalous biaxiality and pleochroism observed in amethyst quartz is a property of the color center itself and not a property of the α-quartz crystal structure.

Introduction

The color of amethyst quartz has been attributed to color centers related to iron impurity. Berthelot (1906) recognized this as a radiation color; it is bleached by heating the crystals at ~400°C, but restored upon re-irradiation by gamma rays, X-rays, or other ionizing radiation. A detailed review of the optical and other properties of amethyst-quartz including literature references through 1960 was published by Frondel (1962).

Basal (0001) sections of amethyst-colored α-quartz crystals display a weak anomalous dichroism and biaxial character which is in direct conflict with the holotrigonal symmetry of the α-quartz structure and thus has led to numerous suggestions that the symmetry is lower than holotrigonal. Melanckolin and Tsinober (1936) and others attempted to associate the biaxiality of amethyst with Brazil twinning. The anisotropy they observed in the amethyst EPR spectrum led Barry and Moore (1964) and Barry, McNamara, and Moore (1965) to attribute its biaxiality to non-random substitution of Fe" ions in the equivalent silicon sites. In the present investigation, optical and thermal bleaching experiments removed the observed anisotropy, optical biaxiality, and pleochroism from a basal section of synthetic amethyst crystal, which then became very close to uniaxial. The anisotropy of the optical absorption spectrum of amethyst was observed earlier by Cohen (1956) using plane polarized light.

The view of Barry and co-workers that the biaxiality in amethyst is due to the anisotropic distribution of Fe" ions in positions substitutional for silicon in the α-quartz structure is not completely implausible. However, they attributed the homogeneity of the electron spin resonance and the removal of biaxiality after heating at about 650°C to a redistribution of Fe" ions. It is unlikely that the substitutional Fe" ions can diffuse in the α-quartz structure at 650°C and be evenly redistributed in positions substitutional for silicon without disruption of the structure because of the covalent nature of the cation-oxygen bonds in quartz. To account for the homogeneity of the electron spin resonance and the removal of biaxiality and pleochroism observed after heating, we have to assume that either the Fe" ions responsible are not substitutional for silicon, or the anisotropy observed is also related to an interstitial impurity in conjunction with the substitutional Fe" ions (Hassan, 1970). The biaxial nature of amethyst is without doubt associated with the color-producing centers, and any explanation for the anomalous biaxiality has to account for this association. The role of iron in producing the
amethystine color in α-quartz as well as the nature of
the color centers are given in the following paper
(Cohen and Hassan, 1974).

Experimental

Materials

The specimen used for the anisotropy experiments
was cut from a deeply colored zone of a natural
Brazilian amethyst crystal, Specimen No. R-1454
from the National Museum of Natural History,
Washington, D. C. This specimen was in the form of
a rectangular block whose two pairs of polished
faces permitted the anisotropic absorption measure-
ments to be made perpendicular to both the c and the
*3 axes (Fig. 1). Later, thinner wafers were cut
from the same specimen in order to make measure-
ments in the higher absorbance region in the deep
ultraviolet. The specimens were polished using sil-
icon carbide powders of various grain sizes, and the
final polish was done by alumina lapping powders.
The thickness of the polished specimens were meas-
ured with a Doall micrometer having a metric
vernier scale.

Optical Absorption Measurements

All absorption spectra were measured at room tem-
perature vs air using a Cary double beam recording
spectrophotometer, Model 14R, serial number 1564.
A Cary Model 1471250 light housing containing a
Sylvania Type DSL halogen lamp as the light source
was mounted in place of the standard (visible)
source. All absorption spectra were measured in an
atmosphere of pure dry nitrogen gas to eliminate
water from the optical path and thus water bands
from the near infrared as well as to minimize as
much as possible the absorption in the ultraviolet
region caused by molecular oxygen. A curve ana-
lyzer at Mellon Institute, Carnegie Mellon Univer-
sity, Pittsburgh, Pennsylvania, was used to resolve
the bands.

Measurements Using Polarized Light

In the visible from 3.09 eV and near infrared
regions up to 0.95 eV, the light was polarized by
means of polaroid J-film. For the near ultraviolet,
a Glan prism was used as the polarizer with cutoff
at approximately 4.13 eV. Both the polaroid film
and the prism were fitted into specially constructed
holders allowing their free rotation around 180°.
The dichroic ratio calculated, is defined as:

\[
k_{E(A)/E(B)}
\]

where *A* and *B* are directions of maximum and min-
imum absorption coefficients respectively.

Light from the monochromator is slightly pola-
rized by internal reflection, and, in addition, the
response of the photocells is sensitive to the direc-
tion of the electric vector of the incident light (*E*).
When quantitatively comparing results from different
specimens and different laboratories, it is necessary
to determine the polarization introduced by the
instrument and the sensitivity of the photocell. Since
the present experiments were performed on the same
specimen with the same polarizers and spectro-
photometer, measurements of these variables were
found unnecessary. The reproducibility of the optical
system was checked by determining the absorbance
in a given direction, then rotating both the polarizer
and the sample through 90°. The absorption spectra
were found to be consistent. This shows that the
response of the photocell is the same in the two
directions of the electric vector of the incident light
within the experimental error. In the present investi-
gation the polarizers were always rotated so that
any error due to the nonuniformity of the coloring
material would be eliminated. The procedure fol-
lowed in recording the absorption spectra in pola-
rized light was as described by Cohen and Smith
(1958).

The spectrum observed when the electric vector
in this specimen and consists of three or more bands rather than the one band reported previously for amethyst quartz. The absorption bands are ligand-cation electronic charge transfer transitions of $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ (Cohen and Hassan, 1970), and their clear resolution here is due to the extremely small iron content (83 ppm). The complexity of the absorption in this region (6.2-5.6 eV) is attributed to the existence of $\text{Fe}^{3+}$ in more than one site in the $\alpha$-quartz structure (Cohen and Hassan, 1974). Figure 3 shows the details of the optical absorption spectra of the sample in the visible and near infra-

### Table 1. Position of Absorption Band Maxima in a Natural Amethyst Crystal, Normal Light*

<table>
<thead>
<tr>
<th>Band Designation</th>
<th>Orientation of Specimen</th>
<th>Energy in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-α</td>
<td>$\perp c$</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>6.26</td>
</tr>
<tr>
<td></td>
<td>$\parallel r$</td>
<td>6.20</td>
</tr>
<tr>
<td>2-β</td>
<td>$\perp c$</td>
<td>5.63</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>5.63</td>
</tr>
<tr>
<td></td>
<td>$\parallel r$</td>
<td>5.60</td>
</tr>
<tr>
<td>3-γ</td>
<td>$\perp c$</td>
<td>5.15</td>
</tr>
<tr>
<td>4-δ</td>
<td>$\parallel c$</td>
<td>4.96</td>
</tr>
<tr>
<td>5-ξ</td>
<td>$\perp c$</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>$\parallel r$</td>
<td>3.54</td>
</tr>
<tr>
<td>6-ζ</td>
<td>$\perp c$</td>
<td>3.023</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>3.023</td>
</tr>
<tr>
<td></td>
<td>$\parallel r$</td>
<td>3.023</td>
</tr>
<tr>
<td>7-θ</td>
<td>$\perp c$</td>
<td>2.285</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>$\parallel r$</td>
<td>2.40</td>
</tr>
<tr>
<td>8-**</td>
<td>$\perp c$</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>1.60</td>
</tr>
<tr>
<td>9-κ complex</td>
<td>$\perp c$</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>$\parallel c$</td>
<td>***</td>
</tr>
<tr>
<td></td>
<td>$\parallel r$</td>
<td>***</td>
</tr>
</tbody>
</table>

* Smithsonian Institution, No. R1454
** A weak band possibly due to a spin forbidden transition of the $\text{Fe}^{3+}$ ion.
*** Broad complex absorption in the 1.50-1.00 eV region.
red regions before cutting from it the thinner wafers used in measurements illustrated in Figure 2. Thin wafers were necessary because of the high light absorbance in the ultraviolet region.

It is clear from studying Figures 2 and 3 that 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.

The Amethyst Color and Biaxiality

A basal section (0.167 cm thick) cut from the specimen and exhibiting a biaxial angle \(\sim 10^\circ\) (9–11\(^\circ\)) was heated in air. The amethyst color remained essentially unchanged to 280\(^\circ\)C, a very slight fading was first noticeable at 300\(^\circ\)C, and at 390\(^\circ\)C the amethyst color completely disappeared\(^2\). The biaxial angle became \(\sim 3^\circ\) after bleaching. Upon exposure to X-rays, a faint but clear amethystine color started developing in the first few minutes of irradiation and became deeper during further exposure (1.5 hours). The \(\theta\) band, the main band in the visible region, increased in intensity as depth of the amethyst color increased (Cohen and Hassan, 1974). The biaxial angle increased to \(\sim 10^\circ\) after recoloration. Optical bleaching, using light from a Hg-Xe lamp whose peak intensity is at 2537 Å, had an effect similar to thermal bleaching, on a basal section of natural amethyst.

Anisotropy of Absorption in the Basal Plane

Figure 4 shows the polarized absorption spectra for the main band (\(\theta\) band) in the visible region centered at 2.285 eV with the incident light along the \(c\) axis. Curve 1 in Figure 4 refers to a measurement with \(E\) vibrating parallel to the direction of

\*Both \(\theta\) and \(\xi\) bands also disappeared. A detailed study of the fading characteristics upon heating and growth curves of the amethyst bands upon re-irradiation with X-rays has been done by Hassan (1970).
maximum absorption coefficient, curve 2 is in normal light, and curve 3 is with E vibrating parallel to the direction of minimum absorption coefficient. The integrated absorption in the θ band is greater when E vibrates in the direction of the a2 axis than when it vibrates perpendicular to it in this specimen orientation. The magnitude of the anisotropy is given by the value of the dichroic ratio in Table 2. The insert spectrum shows how the absorbance of the θ band changes with change of the orientation of the electric vector of the incident radiation (E). The insert spectrum was obtained by rotating E at the wavelength of the maximum of the θ band in normal light (2.285 eV) in the a plane where the a2 axis is the 0° orientation. Data were taken every 5°. A maximum absorption for E at +60° and a minimum for E at -30° from a3 was observed.

Curve 1 in Figure 5a is the spectrum with E vibrating perpendicular to the a1 axis, curve 2 is the spectrum with E vibrating parallel to the a1 axis. The anisotropy of the ξ and η bands in the near ultraviolet is illustrated in Figure 5 (b and c, respectively). The η band has absorption maxima for E at +60° and at +30° to reference direction a3 as well as two minima at -30° and -60°. The polarization orientation at +60° and -30° is the same as that observed in the adjacent θ band, and could possibly be due to overlapping of these bands. The other polarization orientation observed at +30° and -60° from the reference direction might also correspond to that of the very close ξ band.

The broad absorption in the vicinity of 1.3 eV in Figure 6 was studied in the same way. This band is attributed to the 5T2g (5D) 4Eg (5D) spin-allowed transition of Fe2+ in an interstitial octahedral environment. The absorption in this region is quite complex. It has been previously observed that this absorption is split into two components in a more ionic environment (Cotton and Meyers, 1960). This splitting is considered to be due to a dynamic Jahn-Teller effect in the excited 4Eg state. In the quartz structure it was found to be composed not only of bands having maxima at 1.34 eV and 1.265 eV, but also several minor bands (Fig. 6) using different orientations of the electric vector of polarized light.

Figure 7 shows the polarized absorption spectra of Brazilian amethyst in the near infrared region. Curve 1 is the spectrum with E of the incident radiation vibrating parallel to the direction of the experimental maximum, curve 2 is the spectrum with E vibrating in the direction of the exhibited minimum, and curve 3 is in normal light. An approximate gaussian resolution of the spectra suggests that the absorption in the 1.3 eV region consists of three different bands with peaks at about 1.45, 1.28, and 1.14 eV in normal light (Figure 8a). The bands have different anisotropies and their energy values at the peaks shift for different orientations of the electric vector of the polarized light. Figures 8b and 8c show the resolved polarized spectra measured in the direction of maximum and minimum absorption coefficients respectively. The band around 1.67 eV in normal light (Fig. 8a) also contributes to the absorption in this spectral region. The existence of more than one band makes this optical region very complex, and for this reason the band is labelled kcomplex. The anisotropy it exhibits, as illustrated in the insert of Figure 7, is actually a summation of the anisotropies of several bands.

### Table 2. Properties of the Optical Bands in a Natural Amethyst Crystal

<table>
<thead>
<tr>
<th>Band</th>
<th>Normal Incidence on Plate Cut</th>
<th>Band maximum normal light (eV)</th>
<th>Orientation of E at maximum absorption</th>
<th>Orientation of E at minimum absorption</th>
<th>Angle between max. and min. absorption (°)</th>
<th>Dichroic ratio kmax/kmin</th>
<th>Energy Shift of band maximum (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ξ</td>
<td>⊥ σ</td>
<td>3.54</td>
<td>+60° from a3</td>
<td>-30° from a3</td>
<td>90°</td>
<td>1.11</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>⊥ a3</td>
<td>3.48</td>
<td>+60° from a3</td>
<td>-60° from a3</td>
<td>90°</td>
<td>1.13</td>
<td>0.12</td>
</tr>
<tr>
<td>η</td>
<td>⊥ σ</td>
<td>3.02</td>
<td>+60° from a3</td>
<td>-30° from a3</td>
<td>90°</td>
<td>1.25</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>⊥ a3</td>
<td>2.28</td>
<td>+60° from a3</td>
<td>-60° from a3</td>
<td>90°</td>
<td>1.24</td>
<td>0.06</td>
</tr>
<tr>
<td>θ</td>
<td>⊥ σ</td>
<td>2.27</td>
<td>+60° from a3</td>
<td>-30° from a3</td>
<td>90°</td>
<td>1.34</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>⊥ a3</td>
<td>1.30</td>
<td>+60° from a3</td>
<td>-60° from a3</td>
<td>90°</td>
<td>1.10</td>
<td>0.02</td>
</tr>
</tbody>
</table>
It is clear from the observations described, that the absorption of light normally incident on a basal section of an amethyst-colored α-quartz crystal is highly anisotropic. Similar orientations in uncolored α-quartz are isotropic.

**Anisotropy of Absorption Parallel to the c Axis**

The anisotropy of light absorption in the bands described above was also studied in a specimen cut perpendicular to the a axis. Data for the visible and the near infrared regions were obtained, and the results are shown in Table 2.

The anisotropy of the ζ, η, and θ bands in the same specimen shows a maximum absorbance where E vibrates parallel to the c axis, and a minimum when E vibrates perpendicular to the c axis. The κ-complex band although exhibiting a weak absorption in the orientation parallel to the c axis is still strongly anisotropic. An absorption maximum is observed when E vibrates along a direction 45° on either side of the c axis (Fig. 9). Absorption minima are observed when E vibrates, either parallel or perpendicular to the c axis. The direction of maximum absorption conforms with the direction of channels in the α-quartz structure (Hassan, 1970).

**Discussion of Results**

The experiments described above indicate that the absorption bands in amethyst α-quartz are anisotropic. The anisotropic absorption of plane-polarized light by the absorbing centers indicates that the wave function of at least one of the states involved in each center has directional properties. It was noticed that these directional properties have a marked relationship to the α-quartz structure in regard to both the channels and specific crystal-
bands was found to be dependent on the direction of the electric vector of the incident radiation, on the orientation of the section under investigation, and on the amount of absorption present in adjacent bands. The energy shift of the absorption bands with polarized light was calculated and is given in Table 2.

The dichroic ratios for several of the bands observed calculated from the expression previously defined are given in Table 2.

Absorption Indicatrix

The absorption coefficient is defined by Blakney and Dexter (1954) by the following expression:

$$\kappa(E, \omega) = \frac{2\pi \eta h c W_{\nu}}{V k_0 \omega |A_0|^2}\ \text{cm}^{-1}$$

where $h\omega$ is the energy of the quantum of light incident on a crystal of volume $V$, dielectric constant $k_0$, and index of refraction $\eta$, and where $|A_0|^2$ is the square of the amplitude of the vector potential associated with the absorption bands.

**Fig. 6.** The polarized absorption spectra of Brazilian amethyst in the near infrared. Dotted curve refers to the absorption in normal light, the remainder of the curves refer to different orientations of $E$ as indicated. The reference direction is the $a_3$ axis.

**Fig. 7.** The anisotropic absorption of Brazilian amethyst in the near infrared region. The insert spectrum illustrates the change in the optical density of the $K_{\text{complex}}$ bands with changing orientation of $E$. 

lographic directions. The bands differ in anisotropy and in most cases have directions of absorption maxima and minima at right angles to each other (Table 2).

The energy at the absorption peak of the different
Fig. 8. An approximate gaussian resolution of the summation absorption curves of Brazilian amethyst in the near infrared region illustrated in Figure 7. (a) Spectrum in normal light; (b) spectrum in the direction of minimum absorption coefficient; (c) spectrum in the direction of maximum absorption coefficient.

associated with the radiation field of the quantum. \( W_{\gamma} \)
is the probability per unit time that the quantum is absorbed by the crystal, and the rate at which energy is absorbed per unit volume is given by \( (h\omega/V) W_{\gamma} \). All the described experiments were performed on the same polished wafer of amethyst, using the same source of radiation. Therefore, at a given wavelength, the absorption coefficient is directly related to the index of refraction.

In order to illustrate how the absorption coefficients of the optical bands in amethyst vary according to the vibration direction of the electric vector of the incident light and to learn about the orientation of the absorbing centers, an orderly frame was constructed and will be referred to as the absorption indicatrix. It is used here as a method for interpreting the observed optical absorption. In isotropic media, the absorption coefficient will not change with the vibration direction of the electric vector of the incident light at a given wavelength. The interaction of the highly ordered atoms with the light waves would result in cancellation of any directional effect. Consequently, all the vectors relating the absorption coefficient to vibration directions are of equal length, and the expected isotropic absorption indicatrix is a sphere. Basal sections of \( \alpha \)-quartz, being perpendicular to the optic axis, are isotropic. However, within a basal section of amethyst-quartz the tips of the vectors (absorption coefficients) for the \( \theta \) band do not fall along a circle, as might be expected, but along an ellipse. Thus light travelling along the \( c \) axis in an amethyst section, is resolved into two polarized components vibrating at right angles to each other. The difference in magnitude, (one is a minimum, \( k_{\sigma_1} \), and the other is a maximum \( k_{\sigma_2} \)), indicates a directional effect that results from either a change in the atomic arrangement (crystal symmetry) or the presence of some foreign configuration different from the regular one. Knowing that no major deviation from the \( \alpha \)-quartz structure has been detected in amethyst, we can conclude that the anisotropy observed in the optical absorption in the \( \theta \) band is due to the presence of a foreign configuration having a directional electron density. The \( \zeta \) band in amethyst, having a different energy value than the \( \theta \) band, also shows similar anisotropic behavior but has a different polarization orientation, its maximum and minimum differing in position from those for the \( \theta \) band.

For light vibrating parallel to the \( c \) axis, the absorption coefficient \( k_{\pi} \) in both the \( \theta \) and \( \zeta \) band peaks was found to be greater than in any other orientation observed.

*Proposed Symmetry for the \( \theta \) and \( \zeta \) Bands*

The crystallographic axis, \( c \), can no longer be called the optic axis in regard to the color center,
since light vibrating along its direction (in the 2.285 and 3.54 eV regions) is resolved into more than one component. The values of the absorption coefficients in the principal directions $k_{\sigma_1}$, $k_{\sigma_2}$, and $k_{\pi}$ can be described for three mutually perpendicular vibration directions where $k_{\sigma_1} \neq k_{\sigma_2} \neq k_{\pi}$. These results suggest symmetry no higher than orthorhombic for the color center or centers responsible for the absorption in amethyst in the visible and near ultraviolet regions since the centers are of a biaxial nature, with the crystallographic c axis as their acute bisectrix.

**Conclusions**

The anomalous biaxiality and pleochroism observed in amethyst crystals are attributed to the existence of color centers with symmetry no higher than orthorhombic. Bleaching the amethyst sections either thermally or optically results in the disappearance of both the $\theta$ and $\xi$ bands responsible for the amethyst color. The basal section then appears to be very close to uniaxial. The amethystine color, biaxiality, and pleochroism reappear upon exposure to ionizing radiation. It is therefore obvious that it is the optical color centers that depart from the normal quartz symmetry, not the quartz structure as a whole (as suggested by Pancharatnam, 1954) that is different in amethyst than in other $\alpha$-quartz.

This work thus explains why the symmetry obtained from optical measurements differs from the symmetry obtained by X-ray measurements. The anisotropy of these color centers is attributed to the existence of a directional electron density, which conforms with the crystallographic directions or the channels in the $\alpha$-quartz structure. In the basal section of the specimen investigated, the electron density (in the $\theta$ band region) is oriented in the direction of the $a_2$ axis. This observation supports the idea that a selective substitution for Si$^+$ by Fe$^{3+}$ is the actual precursor of the color center (Barry and co-workers, 1964, 1965). However, in a section cut perpendicular to the $a_3$ axis, the electron densities of several centers absorbing in the $\xi$, $\theta$, and $k_{\text{complex}}$ band regions are oriented in the directions of the existing channels in the structure, which indicates that interstitial impurity is involved in the process of the color center production. A detailed study of the nature of the iron centers in $\alpha$-quartz is discussed in the following paper (Cohen and Hassan, 1974).

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References


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