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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^{3+} compounds, 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 biaxialty 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^{3+} 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^{3+} 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^{3+} ions. It is unlikely that the substitutional Fe^{3+} 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^{3+} ions responsible are not substitutional for silicon, or the anisotropy observed is also related to an interstitial impurity in conjunction with the substitutional Fe^{3+} 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

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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 measurements to be made perpendicular to both the *c* and the a_3 axes (Fig. 1). Later, thinner wafers were cut from the same specimen in order to make measurements in the higher absorbance region in the deep ultraviolet. The specimens were polished using silicon carbide powders of various grain sizes, and the final polish was done by alumina lapping powders. The thickness of the polished specimens were measured with a Doall micrometer having a metric vernier scale.

Optical Absorption Measurements

All absorption spectra were measured at room temperature *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 analyzer at Mellon Institute, Carnegie Mellon University, Pittsburgh, Pennsylvania, was used to resolve the bands.

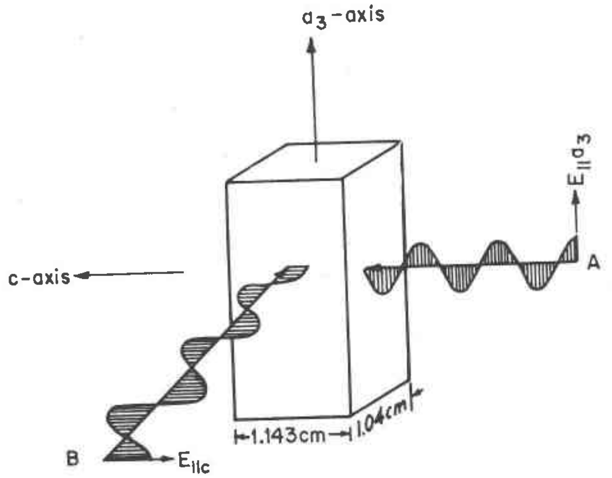

FIG. 1. Orientation and dimensions of the Brazilian amethyst specimen used in the absorption experiments. **A** and **B** show the normal incidence of polarized rays on planes cut perpendicular to the *c* axis and to the a_3 axis, respectively.

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:

$$k_{E(A)}/k_{E(B)}$$

where A and B are directions of maximum and minimum absorption coefficients respectively.

Light from the monochromator is slightly polarized by internal reflection, and, in addition, the response of the photocells is sensitive to the direction 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 spectrophotometer, 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 investigation the polarizers were always rotated so that any error due to the nonuniformity of the coloring material would be eliminated. The procedure followed in recording the absorption spectra in polarized light was as described by Cohen and Smith (1958).

The spectrum observed when the electric vector

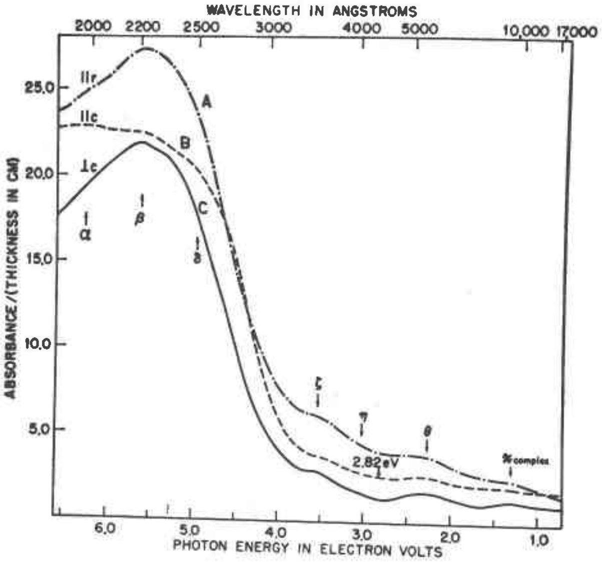

FIG. 2. Absorption spectra of Brazilian amethyst for normal incidence on planes cut (**A**) parallel to a positive rhombohedral face (*r*), (**B**) perpendicular to the a_3 axis, (**C**) perpendicular to the *c* axis. Measurements were taken using normal light.

(**E**) of the incident light is parallel to the optic axis *c*, is called the π-polarized spectrum. The σ-spectrum is observed when **E** is perpendicular to the optic axis. Other directions of **E** are marked on the appropriate spectra in the figures. The slightly polarized light of the spectrophotometer system not intentionally polarized by use of polaroid film or polarizing prism is referred to as normal light.

Channels in α-Quartz Crystals

A model of the α-quartz crystal structure reveals the often described channels parallel to the *c* axis and those parallel to the *a* axis. In addition, other channels through the structure run perpendicular to the positive rhombohedral (*r*) faces and, in the *c-a* axial planes, at 45° on both sides of the *c* axis (Hassan, 1970).

Anisotropic Optical Absorption Bands of a Natural Brazilian Amethyst-Quartz Crystal

Figure 1 shows the dimensions, orientation, and interrelationships of the plane-oriented directions in the crystal studied. The resultant absorption spectra at room temperature exhibit a number of overlapping bands—labelled α, β, δ, ζ . . . (Fig. 2)—with absorption maxima located as summarized in Table 1. The band at 6.2 eV has not been previously reported in the literature. That at 5.6 eV is clearly resolved 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 $O^{2-} \rightarrow Fe^{3+}$ (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 Fe^{3+} in more than one site in the α-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*

Band Designation	Orientation of Specimen	Energy in eV
1-α	⊥c	6.14
	||c	6.26
	||r	6.20
2-β	⊥c	5.63
	||c	5.63
	||r	5.60
3-γ	⊥c	5.15
4-δ	||c	4.96
5-ξ	⊥c	3.54
	||c	3.54
	||r	3.54
6-η	⊥c	3.023
	||c	3.023
	||r	3.023
7-θ	⊥c	2.285
	||c	2.27
	||r	2.40
8-**	⊥c	1.65
	||c	1.60
9-κ complex	⊥c	1.30
	||c	***
	||r	***

* *Smithsonian Institution, No. R1454*
** *A weak band possibly due to a spin forbidden transition of the Fe^{2+} ion.*
*** *Broad complex absorption in the 1.50-1.00 eV region.*

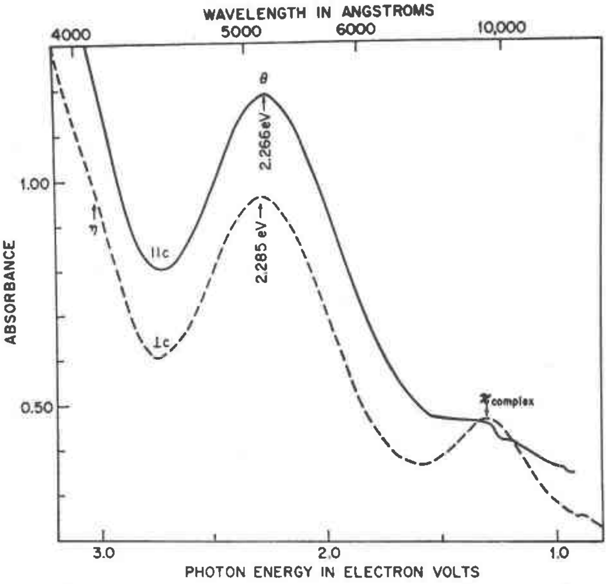

FIG. 3. Absorption spectra of the amethyst specimen illustrated in Figure 2 showing the details of the visible and near infrared regions using normal light.

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 ~10° (9–11°) was heated in air. The amethyst color remained essentially unchanged to 280°C, a very slight fading was first noticeable at 300°C, and at 390°C the amethyst color completely disappeared[2]. The biaxial angle became ~3° 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 θ 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 ~10° 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 (θ 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

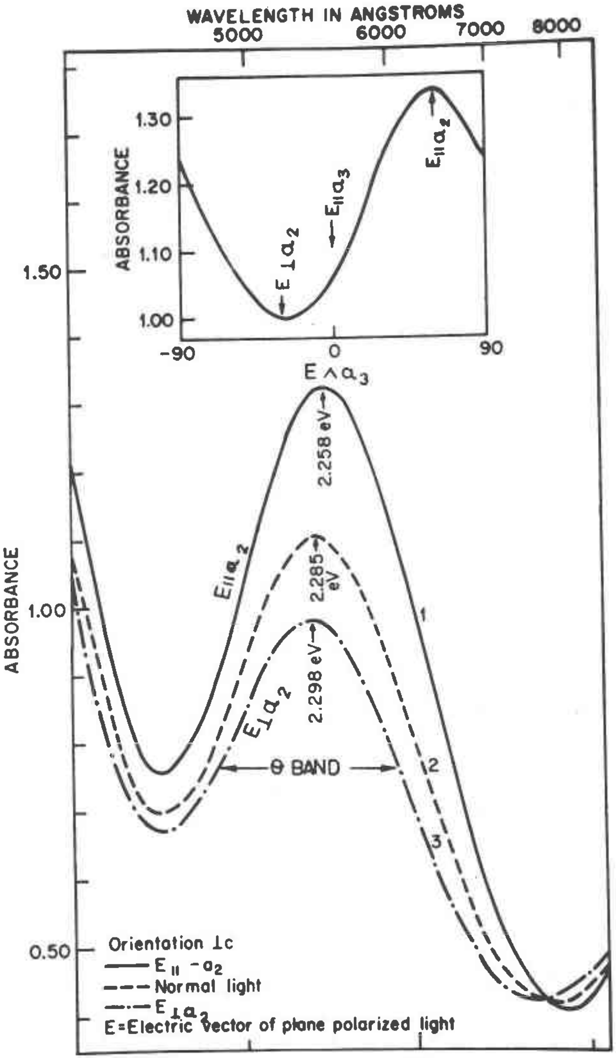

FIG. 4. The polarized absorption spectra of Brazilian amethyst in the visible region for light normally incident on a basal section if (A) the light is plane-polarized with **E** parallel to a_2, (B) normal, or (C) plane-polarized with **E** perpendicular to a_2. The insert spectrum illustrates the change in optical density of the main band with changing orientation of **E**.

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[2] Both θ and ζ 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).

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

Band	Normal Incidence on Plate Cut	Band maximum normal light (eV)	Orientation of E at maximum absorption	Orientation of E at minimum absorption	Angle between max. and min. absorption (o)	Dichroic ratio k_{max}/k_{min}	Energy Shift of band maximum (eV)
ξ	$\perp c$	3.54	+60° from a_3	−30° from a_3	90°	1.11	0.10
			+30° from a_3	−60° from a_3	90°	1.13	
	$\perp a_3$	3.48	parallel to c	perpendicular to c	90°	1.40	0.02
η	$\perp c$	3.02	+60° from a_3	−30° from a_3	90°	1.25	0.04
			+30° from a_3	−60° from a_3	90°	1.24	
	$\perp a_3$		parallel to c	perpendicular to c	90°	1.92	
Θ	$\perp c$	2.28	+60° from a_3	−30° from a_3	90°	1.34	0.04
	$\perp a_3$	2.27	parallel to c	perpendicular to c	90°	1.06	0.00
$\kappa_{complex}$	$\perp c$	1.30	+70° from a_3	+20° from a_3		1.20	0.018
	$\perp a_3$	1.30	+45° from c	parallel to c		1.10	0.02

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 a_2 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 a_3 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 a_3 was observed.

Curve **1** in Figure 5a is the spectrum with **E** vibrating perpendicular to the a_1 axis, curve **2** is the spectrum in normal light, and curve **3** is the spectrum with **E** vibrating parallel to the a_1 axis. The anisotropy of the ζ 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 a_3 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 ζ 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 ${}^5T_{2g}$ (${}^5D$) ${}^5E_g$ (${}^5D$) spin-allowed transition of Fe^{2+} 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 ${}^5E_g$ 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 electrio 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 $\kappa_{complex}$. The anisotropy it exhibits, as illustrated in the insert of Figure 7, is actually a summation of the anisotropies of several bands.

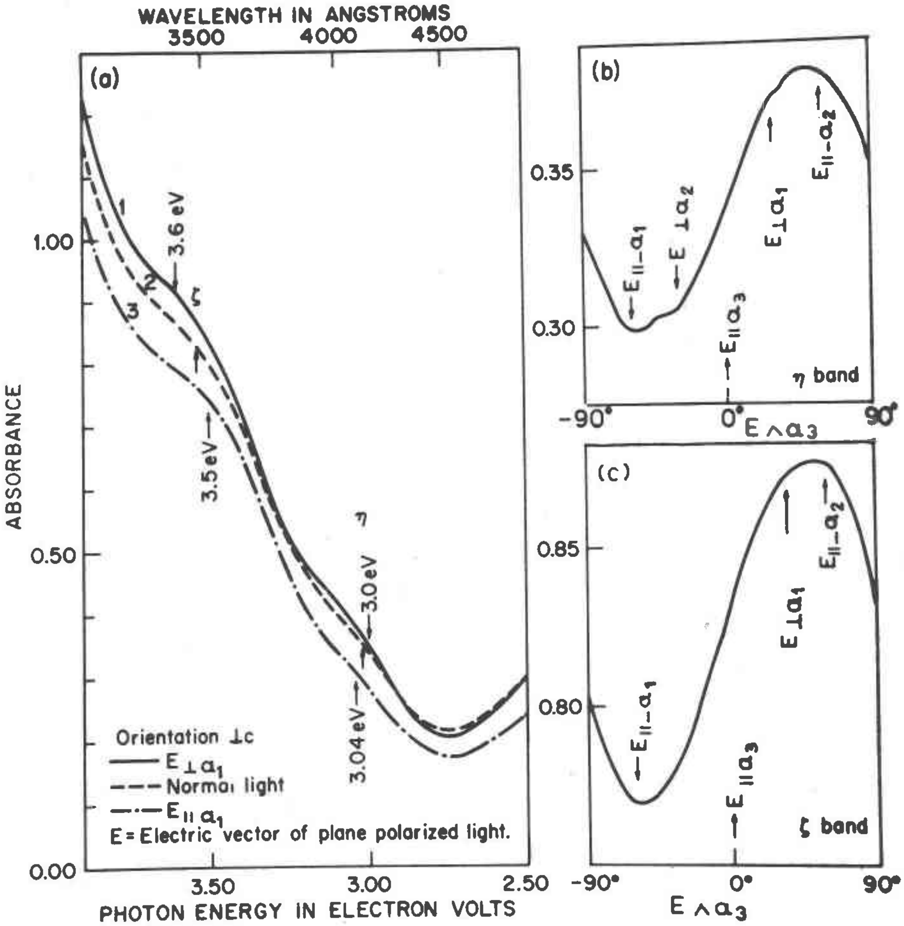

FIG. 5. (a) The polarized absorption spectra of Brazilian amethyst in the near ultraviolet; (b) and (c) illustrate the change in the optical density of the ζ and the η bands by changing orientation of **E**.

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-

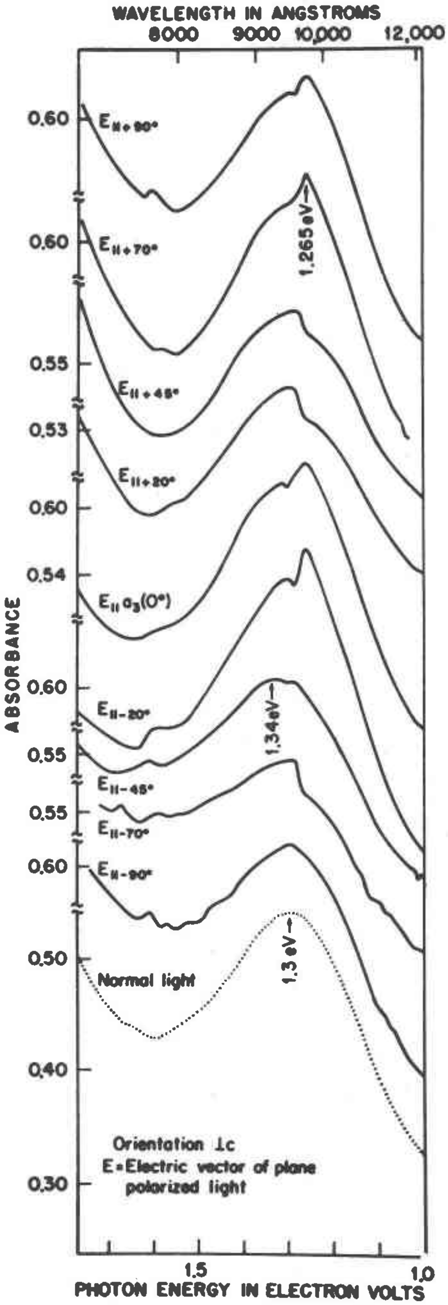

FIG. 6. The polarized absorption spectra of Brazilian amethyst in the near infrared. Dotted curve refers to the absorption in normal light, the remainder of the curves refer to different orientations of **E** as indicated. The reference direction is the a_3 axis.

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 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:

$$= \frac{2\pi\eta h^2 c W_{if}}{V k_0 h\omega \, |A_0|^2} \text{ cm}^{-1}$$

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 η, and where $|A_0|^2$ is the square of the amplitude of the vector potential asso-

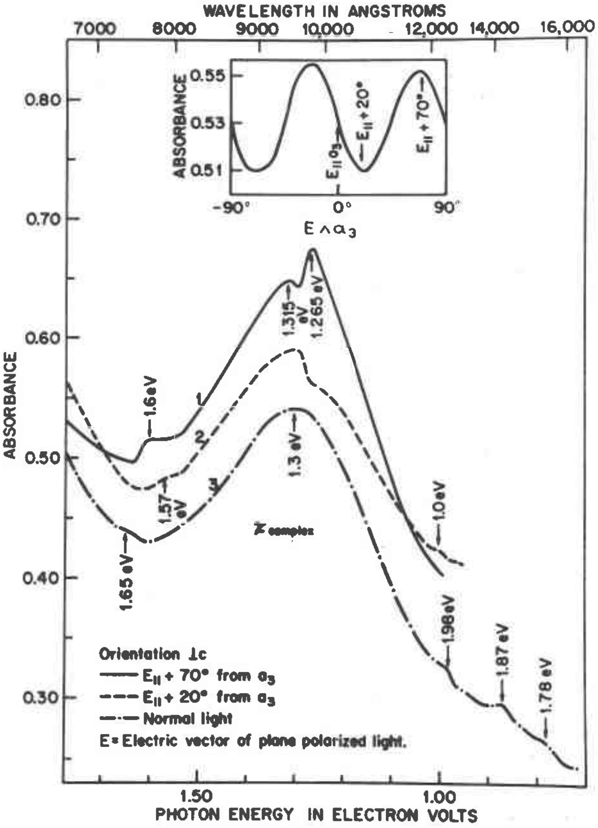

FIG. 7. The anisotropic absorption of Brazilian amethyst in the near infrared region. The insert spectrum illustrates the change in the optical density of the κ_{complex} bands with changing orientation of **E**.

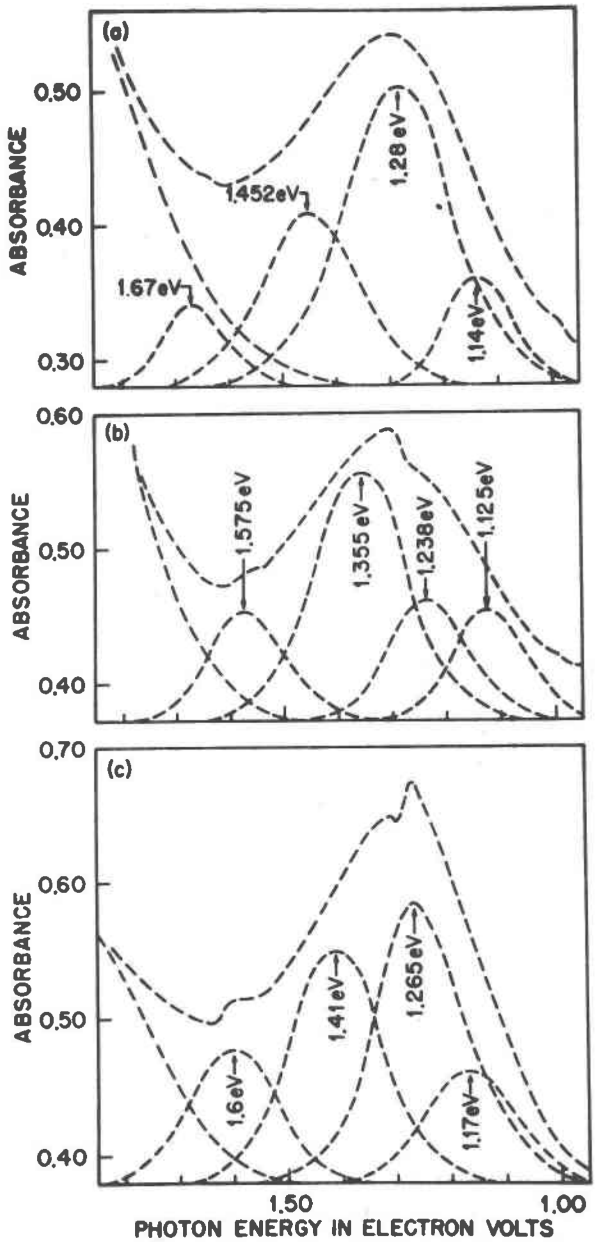

FIG. 8. An approximate gaussian resolution of the summation absorption curves of Brazilian amethyst in the near infrared region illustrated in Figure 7. (a) Spectrum in normal light; (b) spectrum in the direction of minimum absorption coefficient; (c) spectrum in the direction of maximum absorption coefficient.

ciated with the radiation field of the quantum. W_{if} 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 $(h\omega/V)\ W_{if}$. 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 α-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 θ 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 α-quartz structure has been detected in amethyst, we can conclude that the anisotropy observed in the optical absorption in the θ band is due to the presence of a foreign configuration having a directional electron density. The ζ band in amethyst, having a different energy value than the θ band, also shows similar anisotropic behavior but has a different polarization orientation, its maximum and minimum differing in position from those for the θ band.

For light vibrating parallel to the c axis, the absorption coefficient $k\pi$ in both the θ and ζ band peaks was found to be greater than in any other orientation observed.

Proposed Symmetry for the θ and ζ Bands

The crystallographic axis, c, can no longer be called the optic axis in regard to the color center,

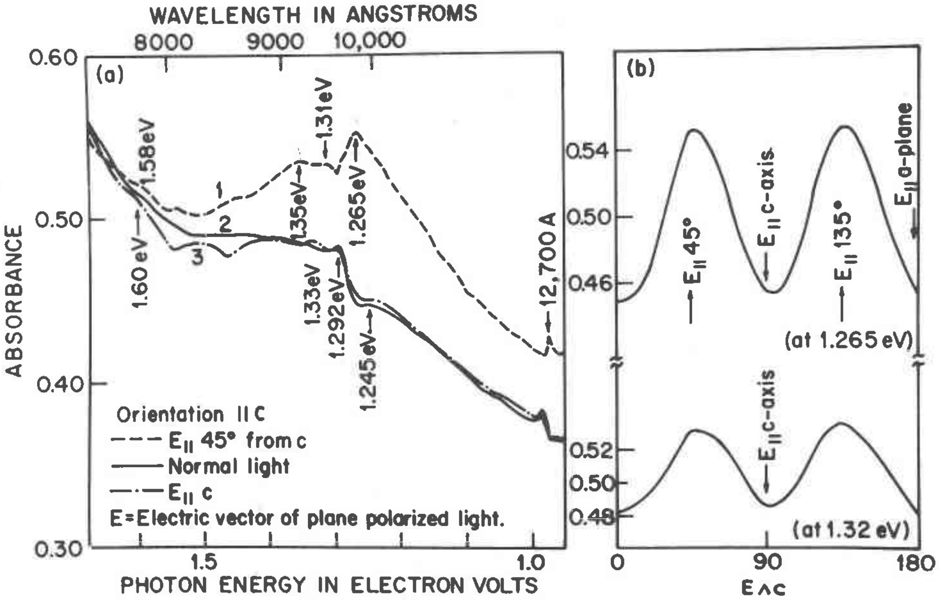

FIG. 9. (a) The anisotropic absorption in the near infrared region of Brazilian amethyst for normal incidence of light on a section cut perpendicular to the a_3 axis. (b) The pleochroism κ_{complex} band at different orientations of **E**, at the two different energies indicated.

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 θ and the ζ 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 α-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 α-quartz structure. In the basal section of the specimen investigated, the electron density (in the θ band region) is oriented in the direction of the a_2 axis. This observation supports the idea that a selective substitution for Si^{4+} 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 ζ, θ, and κ_{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 α-quartz is discussed in the following paper (Cohen and Hassan, 1974).

Acknowledgments

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