

Dynamic biaxial absorption spectra of Ti^{3+} and Fe^{2+} in a natural rose quartz crystal

A. J. COHEN AND L. N. MAKAR*

Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, U.S.A.

ABSTRACT. The absorption spectrum of Ti^{3+} in quartz is typical for that element in an octahedral site, except for the high oscillator strength of the band which indicates intensive charge transfer, most likely between a substitutional Ti^{4+} and an interstitial Ti^{3+} . The biaxial anisotropy of the band is similar to that of octahedral Fe^{2+} in the same crystal, suggesting the same site for the Ti^{3+} , an interstitial site at the intersection of the threefold axis with two twofold axes. The dynamic nature of the Ti and Fe ions is indicated when the crystal is subjected to X-irradiation and then to bleaching treatment with UV-light or heat. $Ti(IV)$ ions are acceptors of electrons donated by Fe^{2+} during X-irradiation. This is indicated by increase of the 2.4 eV band intensity with decrease in the Fe^{2+} band intensities and appearance of Fe^{3+} charge transfer bands in the UV-region. Heat and UV-light treatment decrease the Fe^{3+} CT bands and increase the Fe^{2+} crystal-field bands along with decrease in the 2.4 eV band related to titanium.

KEYWORDS: absorption spectra, titanium, iron, quartz.

ALPHA-QUARTZ is trigonal with the symmetry elements: one threefold c -axis and three twofold axes perpendicular to this axis, a_1 , a_2 , and a_3 . The crystal is optically positive with the high index of refraction along the c -axis. The three Si atoms per unit cell are on tetrahedral sites on three twofold axes. The six oxygen atoms in the unit cell have no symmetry elements. Impurity atoms at tetrahedral silicon sites would be expected to exhibit anisotropic spectra related to the quartz structure, namely the π polarized electronic absorption spectra with the electric vector along the c -axis would absorb more energy (higher electron density) than the σ spectra perpendicular to it with the electric vector in the a -plane.

In the crystals studied in this work, similar to many amethysts, the visible colour is confined to r ($10\bar{1}1$) growth. Brazilian rose quartz specimens sometimes show growth on a core of smoky quartz. This indicates, in these particular cases, an environment that contains ionizing radiation from nearby

radioactive material, allowing the aluminum hole centres responsible for the smoky colour to form. The same radiation could be responsible for the rose colour by reduction of some of the Ti^{4+} present to Ti^{3+} . For Ti^{3+} to be present in quartz, either growth under reducing conditions or colouration by radiation-reduction must take place.

Lehmann (1969) was the first to recognize that Ti^{3+} is in an interstitial position in the lattice of quartz since its spectrum is similar to that of Ti^{3+} in an octahedral field. In a substitutional site, the Ti^{3+} would have to be tetrahedral and would not give the optical spectrum observed. Wright *et al.* (1963), based on their ESR studies at low temperature, have proposed a model for Ti^{3+} colour centres in substitutional sites with interstitial alkali or hydrogen acting as a charge compensator ($Ti^{3+} + H^+ = Si^{4+}$). These centres are not stable at room temperature and all tetrahedral titanium would be expected to present as Ti^{4+} at room temperature. Other workers (Isoya and Weil, 1979) have evidence that these tetrahedral Ti^{3+} centres may be stable at room temperature, but no optical bands have as yet been found that may be attributed to tetrahedral Ti^{3+} centres. Indications are, however, that Ti^{4+} originally enters quartz both in tetrahedral substitutional sites and in octahedral interstitial sites. Since most rose quartz contains microscopic to macroscopic rutile, it can be considered to be often saturated with trace titanium. In the crystals studied in this paper, no rutile was detected by light scattering techniques.

The dynamic nature of Ti^{4+} and Fe^{2+} occurring in octahedral sites in lunar and meteoritic augites subjected to beta secondaries from cosmic ray bombardment and ionizing radiation from natural radioactivity has been investigated (Cohen, 1972a and b).

Other workers suggest that the colour of rose quartz is due to a charge transfer mechanism between Fe^{2+} and Ti^{3+} (Smith *et al.*, 1978). Our conclusions concerning the interplay between

* Present address: Department of Physics, University College of Bahrain, Bahrain, Arabian Gulf.

titanium and iron differ from the conclusions in that paper.

Experimental. The single crystals of rose quartz studied were from the Sapucaia pegmatite, Minas Gerais, Brazil, sample NMNH 115272 of the Mineralogy branch of the National Museum of Natural History, Washington, DC. The analyses (Cohen and Makar, 1984) for Ti, 4/10⁶ Si, Fe 11/10⁶ Si, and Al 112/10⁶ Si were performed by Arc Emission methods.

Two specimens were studied, one cut parallel, ($\bar{1}\bar{2}10$), and the other perpendicular to the optic axis of the crystal. Each specimen had parallel faces ground and polished for optical studies. The basal section was 0.37 cm thick and the optic axial section was 0.43 cm thick. Polarized spectrophotometric data were taken using a Glan-Thompson Prism constructed from calcite with an optical cutoff at 5.6 eV (221 nm) and a Cary Model 14R double beam recording spectrophotometer. A General Electric halogen light source was used in the infrared and visible regions. X-irradiations were made with a Picker industrial X-ray unit containing a water-cooled Machlett AEG-50-G type X-ray tube with tungsten target and beryllium window, operated at 45 kV and 35 ma. X-irradiations were carried out at room temperature, 6 cm below the beryllium window. The accumulated X-ray dosage is reported as irradiation time in hours, and arbitrary relative parameter, because of the difficulty in determining the dosage in quantitative terms.

The absorption spectra were measured immediately after X-irradiation and the specimens were transferred to the spectrophotometer in a darkened room to preclude any optical bleaching by fluorescent lighting or sunlight. Time intervals between successive exposures to X-rays were kept as short as possible to minimize possible thermal bleaching at room temperature.

Optical bleaching experiments were performed using an Oriol high-pressure 200 watt Hg-Xe lamp with peak intensity in the 253 nm region. The sample was cooled by a current of air during exposure to the light.

Heat treatments were done in a furnace equipped with a thermocouple, on a large fused-silica block, and the rate of heating did not exceed 5°C per minute. The samples were cooled slowly to room temperature in the closed furnace overnight.

Spectrophotometric studies. The absorption spectra were first studied in normal light using the two polished sections, cut parallel to ($\bar{1}\bar{2}10$) and to (0001). In Table I the band peak positions of the absorption bands are given in electron volts (eV), nanometers (nm), and reciprocal centimetres (cm⁻¹) and compared in the two specimen orientations. The last column gives an attribution of the origin or possible origin(s) of the band. Of the bands observed using normal light only the bands related to crystal field transitions of octahedral Ti³⁺ and Fe²⁺ are positively identified. The individual bands will be discussed where their detailed anisotropy is described.

Table I. Absorption bands in natural rose quartz single crystals observed in normal light

Specimen Orientation	Peak Position			Band Attribution
	eV	nm	cm ⁻¹	
\perp c (0001)	*	*	*	
\parallel c ($\bar{1}\bar{2}10$)	5.45	227	43960	interstitial Fe ³⁺ C.T. (Cohen & Hassan, 1974)
\perp c	4.90	253	39520	0 + Fe ³⁺ C.T.; or Ti related C.T. (Tippins, 1971)
\parallel c	4.88	254	39360	
\perp c	3.25	381	26215	possible Ti ³⁺ - Ti ⁴⁺ C.T. (Jorgensen, 1957)
\parallel c	3.20	387	25810	
\perp c	2.44	508	19680	Ti ³⁺ in distorted interstitial octahedral site (Lehmann, 1969), charge transfer (this paper)
\parallel c	2.40	516	19360	
\perp c	*	*	*	probable Jahn-Teller distortion of Ti ³⁺ in distorted octahedral site, appears only in κ and $\delta \parallel a_2$. Splitting 6415 cm ⁻¹ .
\parallel c	1.68	738	12945	
\perp c	1.30	953	10485	Fe ²⁺ in distorted interstitial octahedral site $5T_{2g}(5D) + 5E_g(5D)$
\parallel c	1.28	968	10325	
\perp c	1.1	1127	8875	probable Jahn-Teller distortion of Fe ²⁺ in distorted octahedral site. Splitting 1610 cm ⁻¹ ($\perp c$) and 2095 cm ⁻¹ ($\parallel c$).
\parallel c	1.02	1216	8230	

*not observed

Anisotropy of absorption bands in the basal plane. It was found that the spectrum of the single crystal was not isotropic in the basal plane but the absorption bands displayed weak biaxial character similar to that observed for amethyst quartz (Hassan and Cohen, 1974).

If the absorption bands have the symmetry of the quartz structure one would expect the spectrum of a sample cut parallel to the *c*-axis with the electric vector in the *a*-plane (σ spectrum) to give the same spectrum as in a basal section of the crystal with normal light or light polarized in any direction in this plane, namely and isotropic spectrum. This was not found to be the case, as one could predict if interstitial ions are involved rather than ions substituting for silicon and having the same valence state, viz Ge⁴⁺ and Ti⁴⁺, and not interacting with interstitial ions.

Fig. 1 gives a detailed spectrum of the 2.44 eV Ti³⁺ band showing the maximum, minimum, and

normal light spectra in the *a*-plane. Detail of the change of absorbance with the angle of the electric vector at 2.44 eV with absorbance recorded every 5° is also shown. These data indicate that the Ti³⁺ ion has an anomalous biaxiality due to its location in the channels of the quartz structure, and to possible charge transfer with a substitutional Ti⁴⁺ cation.

Fig. 2a shows the detailed anisotropy in the *a*-plane of the bands in the near infra-red region at three orientations of E. E \perp *a*₂ being the maximum absorption and E \parallel *a*₂ being the minimum absorption in this region. This is clearly shown with orientation of E measured every 5° at 1.1 eV (fig. 2b), 1.2 eV (fig. 2c), and the average absorbance for 1.1 eV, 1.2 eV, and 1.38 eV bands (fig. 2d).

There is a striking similarity among the anisotropies of these three bands and the 2.44 eV band in the visible region.

It is well established that the Fe²⁺ ion in octahedral coordination has a spin-allowed band

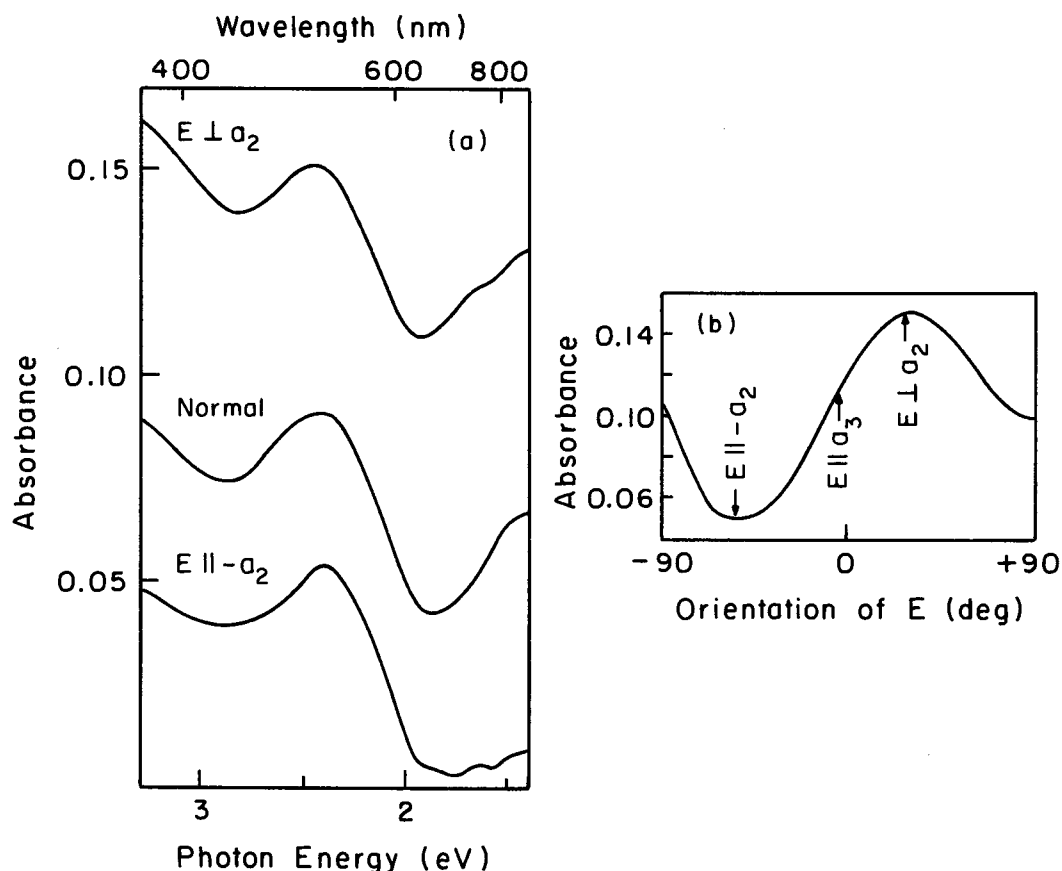


FIG. 1. Absorption spectra of rose quartz basal section: (a) detail in 1.5-3 eV region; (b) change in absorbance of the 2.44 eV band with changing orientation of the electric vector (E).

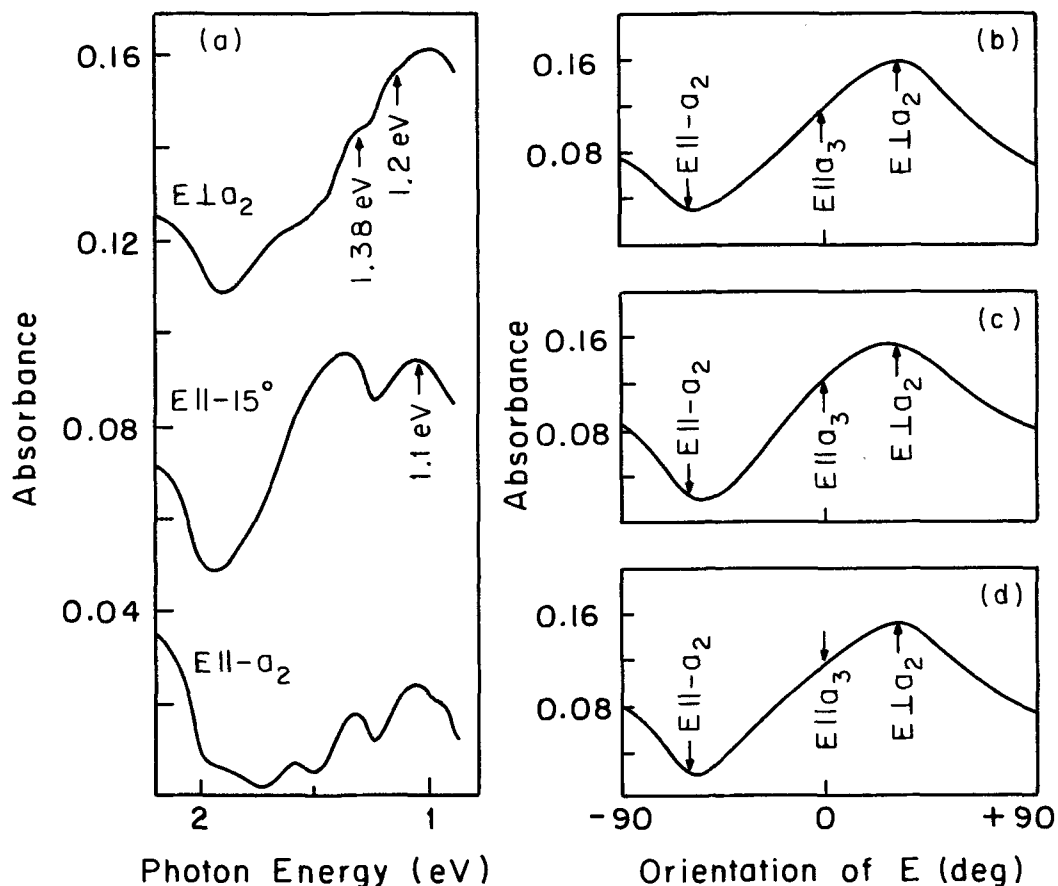


FIG. 2. Absorption spectra of rose quartz basal section: (a) detail in the 1–2 eV region. Change in the absorbance of bands with changing orientation of the electric vector (E); (b) 1.1 eV band; (c) 1.2 eV band; (d) average 1.1, 1.2, and 1.38 eV bands.

in many solids at 1.24 eV. In minerals, the band frequently splits into several overlapping bands caused by distortion of the oxygen polyhedra about the cations from octahedral symmetry. This distortion causes the energy levels of the triply degenerate 5T_g and doubly degenerate 5E_g states to be further resolved, and additional spin-allowed transitions are therefore possible. In the quartz structure with its open channels it seems more reasonable to attribute the complexity of the absorption in the near infra-red region 1.0–1.4 eV to the existence of Fe^{2+} ions in more than one interstitial octahedral site in the lattice with different degrees of distortion.

It is reasonable to expect Fe^{2+} to enter the quartz structure interstitially as it cannot substitute for Si^{4+} with a charge difference of two unless it enters the structure at Fe^{3+} and is later reduced by radiation to Fe^{2+} (Cohen, 1972a). The existence of

voids and channels in the quartz structure can easily accommodate ions of comparatively large radii (Cohen and Hassan, 1974), the position of the complex absorption bands related to Fe^{2+} is in good agreement with the predicted spin-allowed $d-d$ transition for Fe^{2+} in octahedral symmetry. The presence of the Fe^{2+} in interstitial octahedral sites would agree with octahedral Ti^{3+} being in similar sites because of the similarities of the orientations for maxima and minima of the polarized absorption spectra of the two ions in the a -plane. This conclusion is strengthened by the band position of Ti^{3+} and its width at half-maximum in agreement with the earlier work of Lehmann (1969).

Anisotropy of absorption bands in the oriented section cut parallel to the c -axis. Study of the anisotropy in an oriented section parallel to the

c-axis (1 $\bar{2}$ 10) indicates that the 2.4 eV band of Ti³⁺ shows a maximum absorption of light when E vibrates parallel to the *a*-plane and a minimum when E vibrates parallel to *c*. This is anomalous for quartz, which is optically positive, and strongly indicates that the Ti³⁺ is located in the channels in the quartz structure rather than being in a substitutional position. We believe that it is located in the channels and is produced by radiation reduction of Ti⁴⁺ located there as shown by studies described subsequently in this paper. The anomalous anisotropy in the *a*-plane of the Ti³⁺ band at 2.4 eV indicates that the absorbing centres must have higher concentration in this plane or the lobes of the *d*-orbitals responsible for the absorbance are projected in the plane perpendicular to the *c*-axis. Possible substitutional sites for the Ti³⁺ are given by Rinneberg and Weil (1972). There, α and β sites for interstitial Na⁺ are located at the intersections of a threefold axis with two twofold axes. It is believed that the Ti³⁺ and Fe²⁺ ions are located in the α and β sites where the Na⁺ is located in the Rinneberg and Weil model for the substitutional Ti³⁺ centre.

A feature of the π spectrum and the spectrum in normal light is the absorption band at 1.68 eV as shown in Table I. This band is pronounced in the basal section only in $\sigma \parallel a_2$ and is very weak or absent in the $\sigma \perp a_2$ spectrum. Since this band has a minimum absorbance where the 2.4 eV band has a maximum absorbance it would indicate that the major amount of absorption due to Jahn-Teller distortion of the Ti³⁺ ion at 1.68 eV is oriented in π and $\sigma \parallel a_2$ polarizations while the absorption due to the Ti³⁺ transition ${}^2T_{2g} \rightarrow {}^2E_g$ has its maximum absorption in $\sigma \perp a_2$.

Effect of ionizing radiation on spectra. The effect of X-irradiation with time is shown in fig. 3 with

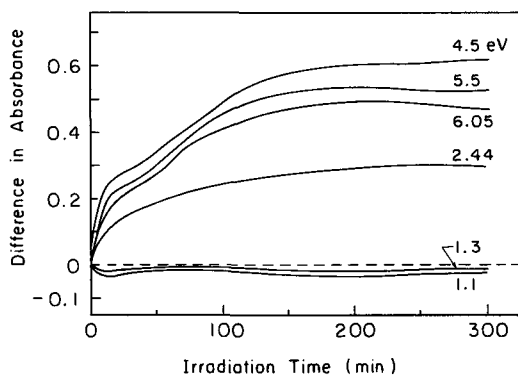
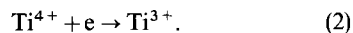
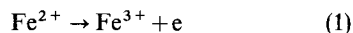


FIG. 3. Change in intensity of absorption band maxima from original colouration during X-irradiation of basal section of rose quartz.

growth in intensity of the 5.5, 4.5, and 2.44 eV bands and decrease in the 1.3 and 1.1 eV band intensities in the section cut perpendicular to the *c*-axis. In addition the well-known band at 6.05 eV, which is due to Fe³⁺ charge transfer, appears. The Fe²⁺ bands (1.3 and 1.1 eV) decrease in intensity with growth of the other bands. The 2.44 eV, Ti³⁺ band growth with decrease in the Fe²⁺ bands indicates an electron donor-acceptor reaction:



The increase in the ultraviolet band region, 6.05–4.5 eV, indicates a growth of two and possibly three Fe³⁺ related bands (Cohen and Hassan, 1974).

Optical bleaching of spectra. The UV light bleaching caused an increase in the intensities of the 1.30 and 1.10 eV bands related to interstitial Fe²⁺ after an initial decrease as shown in fig. 4. The 6.05, 5.50, 4.50, and 2.44 eV bands all show a decrease in intensity with time of bleaching. It is clear that

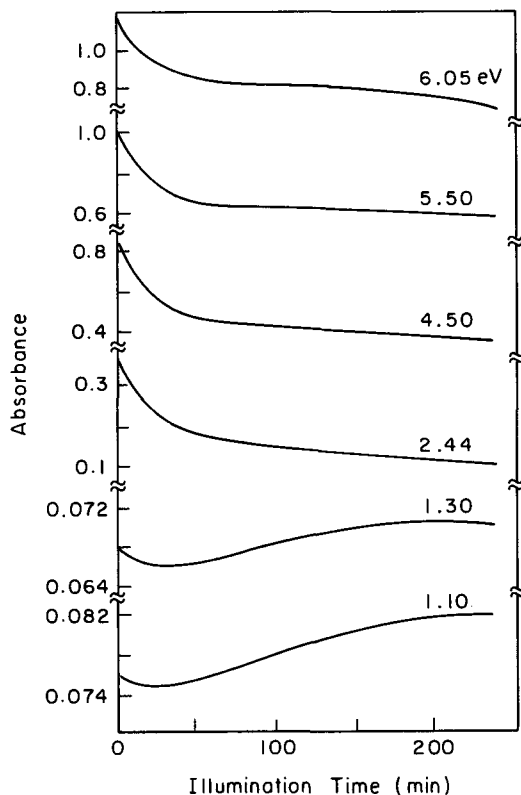


FIG. 4. Changes in intensity of absorption band maxima during illumination with UV light of basal section of rose quartz.

heating and UV illumination of rose quartz reverse the reactions produced by ionizing radiation as shown in equations (1) and (2).

Effect of heating on spectra. Heating at increasing temperature in air causes bleaching of the 2.4 eV band. Fading begins at 200 °C. After heating for 1 hour at 320 °C the band fades completely. Changes in the Fe³⁺ and Fe²⁺ bands were identical with those described under optical bleaching. Re-irradiation with X-rays after heating regenerates the rose colour due to the 2.44 eV band. The Fe³⁺-related band again increases in intensity along with decrease in the Fe²⁺ bands. Heating the quartz above the α - β transition to 650 °C for two hours then slowly cooling to room temperature caused a precipitation of a separate white phase. This phenomenon was earlier observed by Cohen (1960) in impure synthetic quartz. After this high-temperature heat treatment, a prolonged period of X-irradiation resulted in a much fainter rose colour than present previously. This is an indication that a portion of the Ti involved in producing the 2.4 eV band has entered a separate phase. This is further evidence that there was Ti in an interstitial site in the quartz before precipitation.

Charge transfer of Fe²⁺-Ti⁴⁺ versus Ti³⁺-Ti⁴⁺. Smith *et al.* (1978) attribute the band at 2.4 eV (500 nm in their work) to charge transfer between interstitial Fe²⁺ and substitutional Ti⁴⁺ (Fe²⁺ + Ti⁴⁺ → Fe³⁺ + Ti³⁺). Calculation of the oscillator strength of the 2.4 eV band as shown in Table II indeed clearly indicates that it has charge transfer character. Even if one takes into account the possible imprecise nature of emission analysis, the oscillator strength of the band still remains high. After X-ray treatment to saturation of this band the oscillator strength in normal light increases four-fold. Thus there is agreement with Smith *et al.* that charge transfer is involved in producing the band

responsible for the pink colour of rose quartz. The crystal studied by Smith *et al.* differed from the crystal studied in this work in that the Ti content was double, the Fe content four times as high, and the Al more than an order of magnitude greater. In addition, the 2.4 eV band in their crystal was not affected by UV light or ionizing radiation. Thus there is considerable difference in their crystal from the crystal investigated in this work in that our crystal showed increase in the 2.4 eV band with X-irradiation and bleached with ultra-violet light. It is difficult to reconcile Fe-Ti charge transfer with the effects of X-irradiation and their reversal by UV treatment or heating. Namely, why is there a decrease in Fe²⁺ spectra with increase in the 2.4 eV band if the charge transfer suggested by Smith *et al.* is responsible. It seems logical that the 2.4 eV band is increased by oxidation of Fe²⁺ to Fe³⁺ which causes reduction of a Ti⁴⁺ to Ti³⁺. It is suggested, based on our observations that an interstitial Ti⁴⁺ is reduced to Ti³⁺ with the interaction of the latter with nearest neighbour substitutional Ti⁴⁺ to product Ti³⁺-Ti⁴⁺ metal charge transfer. This would be expected to give a higher oscillator strength than Fe-Ti charge transfer and could be expected if interstitial and substitutional Ti⁴⁺ are both originally present.

The difference in the crystal studied here and that of Smith *et al.* indicates that the phenomenon is complex and probably affected by other impurities present such as Al (Cohen and Makar, 1984).

Summary and conclusions. The experiments described clearly demonstrate the anisotropy of the absorption bands in the rose quartz single crystals studied. The anisotropies of the absorption bands in the basal section indicate that the rose quartz crystals unlike pure α -quartz have optical biaxiality which was demonstrated earlier in amethyst quartz (Melankholin and Tsinober, 1963; Barry and Moore, 1964; Barry *et al.*, 1965; Hassan and Cohen, 1974).

If Ti⁴⁺ enters the quartz lattice substitutionally and the subsequent Ti³⁺ centres are produced from these ions then one would expect the absorption of the 2.4 eV band to be a maximum when E parallels the *c*-axis. The electron density was found to be a minimum for this direction and the same holds for the near infra-red bands of Fe²⁺. Wright *et al.* (1963) and Rinneberg and Weil (1972) conclude that a possible site of the Ti³⁺ is a substitutional site along a twofold axis based on the symmetry of ESR lines observed in rose quartz. No direct evidence for substitutional Ti³⁺ in rose quartz single crystals of this study can be observed by absorption spectral measurement. The optical biaxiality and pleochroism of rose quartz in the visible region of the spectrum can be explained by the existence of

Table II. Oscillator Strength of the 2.44 eV Band in Basal Section of Rose Quartz

Orientation	k cm ⁻¹	$W_{1/2}$ * eV	f**
Before X-ray:			
$\sigma_{\parallel a_2}$	0.145	0.82	0.018
$\sigma_{\perp a_2}$	0.409	1.0	0.062
normal light	0.246	1.0	0.037
average $\sigma_{\parallel a_2}$ and $\sigma_{\perp a_2}$	-	-	0.040
After X-ray for 250 minutes:			
normal light	1.030	1.0	0.016

* width at half-maximum of absorption band

** oscillator strength using equation of Dexter (1956)

$N = 1.06 \times 10^{17}$ atoms Ti/cm³.

interstitial Ti in channels or voids of the quartz structure.

The anisotropy in the *a*-plane is a result of unequal filling of the voids in the quartz by Ti. The presence of these positively charged ions located interstitially in the structure must compensate for missing positive charge in the silicon sites. This is most likely due to Al³⁺. The proximity of Fe³⁺ and Ti³⁺ near the aluminum after ionizing radiation treatment precludes the formation of the aluminum colour centre as is the case with massive rose quartz where large quantities of alkali are also present. The neutral alkali produced by ionizing radiation wanders away at room temperature while the Ti and Fe change valence states but remain in their sites; thus the formation of the aluminum colour centre is precluded. The oscillator strength of the 2.4 eV band (Table II) precludes a simple crystal field transition. The intense absorption is most likely between a tetrahedral Ti⁴⁺ and an octahedral Ti³⁺. The decrease of the Fe²⁺ and increase in Fe³⁺ spectra upon treatment with ionizing radiation accompanied by increase in the 2.4 eV band precludes Fe²⁺-Ti⁴⁺ charge transfer as the cause of the 2.4 eV band.

Acknowledgements. We wish to thank John White of the National Museum of Natural History for providing the rose quartz crystals used in this work. The junior author is grateful for a PEO International Peace Scholarship. The work was partially supported by the Provost's fund of the University of Pittsburgh. Dr Diane Wakefield contri-

buted valuable advice concerning the Jahn-Teller distortion of Ti³⁺.

REFERENCES

- Barry, T. I., McNamara, P., and Moore, W. J. (1965) *J. Chem. Phys.* **42**, 2599-606.
 — and Moore, W. J. (1964) *Science*, **114**, 289-90.
 Cohen, A. J. (1960) *J. Phys. Chem. Solids*, **13**, 321-5.
 — (1972a) *The Moon*, **4**, 141-54.
 — (1972b) *The Moon* (D. Reidel Pub. Co., Dordrecht, Holland), IAU Symposium No. 47, 264-78.
 — and Hassan, F. (1974) *Am. Mineral.* **59**, 719-28.
 — and Makar, L. N. (1984) *Neues Jahrb. Mineral. Mh.* 513-21.
 Dexter, D. L. (1956) *Phys. Rev.* **2** **101**, 48-55.
 Hassan, F., and Cohen, A. J. (1974) *Am. Mineral.* **59**, 709-18.
 Isoya, J., and Weil, J. A. (1979) *phys. stat. sol. (a)* **52**, K193-6.
 Jorgensen, C. K. (1957) *Acta Chem. Scand.* **11**, 73-85.
 Lehmann, G. (1969) *Neues Jahrb. Mineral. Abh.* **5**, 222-5.
 Melankholin, N., and Tsinober, L. (1963) *Soviet Physics-crystallography* **8**, 83-4 (Translation of Kristallogr. **8**, 111, 112).
 Rinneberg, H., and Weil, J. A. (1972) *J. Chem. Phys.* **56**, 2019-28.
 Smith, G., Vance, E. R., Hasan, Z., Edgar, A., and Runciman, W. A. (1978) *phys. stat. sol. (a)* **46**, K135-40.
 Tippins, H. H. (1971) *Phys. Rev.* **1**, 126-35.
 Wright, P. M., Weil, J. A., Buch, T., and Anderson, J. H. (1963) *Nature*, **197**, 246-8.

[Manuscript received 18 May 1983;
 revised 6 June 1984]