

MINERALOGICAL MAGAZINE

VOLUME 41 NUMBER 319 SEPTEMBER 1977

Smoky, blue, greenish yellow, and other irradiation-related colors in quartz

K. NASSAU AND B. E. PRESCOTT

Bell Laboratories, Murray Hill, New Jersey 07974

SUMMARY. Almost 400 specimens of natural and synthetic quartz were γ -irradiated and then heated. Polarized absorption spectroscopy, EPR, and spectrochemical analysis were used to investigate the various colors produced.

A blue color originated from absorption by the A_1 and A_2 bands at 1.85 and 2.55 eV. The substitutional Al EPR hole-type center usually considered to be the cause of the color in smoky quartz does not correlate with A_1 and A_2 , but with A_3 , a previously unreported absorption band at 2.90 eV. The A_1 and A_2 absorptions bleach at temperatures as low as 280 °C and as high as 360 °C, the range for A_3 being 140 to 380 °C. The B band at 3.95 eV was previously reported only in irradiated fused silica.

Greenish-yellow colors (appearing yellow when of low intensity) were observed after irradiation (followed by heating in some instances) in many specimens of natural and synthetic quartz; the color originates from the tail of a strong absorption band in the ultraviolet. The bleaching temperature range is the same as that for A_3 .

The wide variation in color of natural and irradiated smoky quartz can be explained by combinations of the smoky (A_3), blue (A_1 and A_2), and greenish yellow absorption features.

THREE colors have been attributed to the effect of irradiation, such as X-rays or γ -rays, on quartz: smoky, amethyst, and greenish yellow.

The smoky designation is usually applied to the range of colors from black through gray and brown to reddish and yellowish tints. These colors have been attributed to the A_1 and A_2 optical absorption bands at 2.0 and 2.6 eV. They have been associated with the so-called aluminum-hole center, a hexet hyperfine-structure electron paramagnetic resonance (EPR) center consisting of an Al^{3+} replacing a Si^{4+} with a hole at one of the neighboring oxygens plus a charge compensating alkali ion or proton near by (Griffiths *et al.*, 1970, among others). There has been some dissatisfaction with the identification of the optical A_1 and A_2 bands with the aluminum-hole center, since the intensities of these two features do not always appear to correlate (e.g. Lell *et al.*, 1966; Halperin and Ralph, 1963). In some irradiated synthetic quartz an 'anomalous pleochroism' (Tsinober, 1962; Tsinober *et al.*, 1967) has been associated with the aluminum-hole center.

The second well-known irradiation-induced color is the amethyst color-center involving Fe (Lell *et al.*, 1966; Chentsova *et al.*, 1966). There is some controversy about the fine details (Lehmann, 1975; Cohen, 1975). This center will not be further discussed.

The third, a recently noted color center, is greenish yellow. This has been produced by the gentle heating of irradiated quartz (Samoilovich *et al.*, 1968); in other instances heating was not necessary (Lehmann, 1971; Lehmann and Bambauer, 1973; Sawyer, 1974, 1976). This color is distinct from yellow citrine and 'greened amethyst' quartz, both allochromatic colorations from Fe (Lehmann and Bambauer, 1973). The greenish shade may not be noticeable at low saturation or in mixtures with a little smoky color.

General reviews on irradiation in quartz have been given by Fröndel (1962) and by Lell *et al.* (1966).

We have found that there are five distinct optical absorption bands in the visible region:

The greenish yellow (abbreviated G-Y) absorption originates from the tail of an intense absorption in the ultraviolet.

The combined A_1 and A_2 bands give a blue coloration; they are centered at 1.85 eV and 2.55 eV with half widths of 0.7 eV and 0.8 eV, respectively; they do not correlate with the aluminum-hole center or with the hextet EPR signal.

The smoky color center originates from a broad band, designated A_3 , at 2.90 eV with a half-width of 1.5 eV; it correlates with the hextet EPR signal and is therefore the aluminum-hole center (Nassau and Prescott, 1975).

And a unique green color absorption was observed in two specimens from Brazil.

Combinations of A_1 and A_2 with some G-Y absorption or a small amount of A_3 absorption (or both) produce blue-green or green colors. The wide variation in color of smoky quartz can now be explained by differences in the relative intensities of these absorption bands. The smoky aluminum-hole center (A_3) absorption occurred only in combination with the other absorptions. Specimens were found, however, that yielded only blue (A_1 and A_2) and only G-Y absorptions.

Experimental

Ten natural smoky quartz specimens, approximately 300 colorless natural, and 73 colorless synthetic (see e.g. Laudise, 1962; Ballman *et al.*, 1966) specimens from many sources were studied. The majority of the natural specimens were undoubtedly from Brazil. Most were quartz crystals, although some massive samples from veins and pegmatite cores were also included. Specimens from identified localities are listed in Table I.

A search was made for green and greenish-yellow clear quartz. Four specimens were located at the Smithsonian: B3919, a greenish-yellow crystal from Minas Gerais, Brazil, in the Carl Bosch collection; 44678A and B (two from a group of crystals, the others being various shades of citrine), collected in Brazil by Dana in 1884; and 3297, a partly heated amethyst ('greened amethyst') from Bahia, Brazil. A greenish yellow quartz, 109570 from Minas Gerais, Brazil, in the Harvard University collection was also studied.

Colorless specimens were irradiated with 15 megarads of γ -rays in a cobalt-60 cell, a saturation dose. All specimens were then annealed in air at 20 °C increments for 2 to 4 hours at each temperature to develop any intermediate colors. Step heating was continued until all samples became colorless. Since the color changes observed on heating are time-, temperature-, and irradiation-dose-dependent, the temperatures in Tables I and II are approximate, no better than ± 30 °C.

Polarized optical absorption spectra were taken at room temperature on a Cary 14R spectrophotometer in the 1 eV to 5.7 eV range (1.2 μm to 0.22 μm). The data were plotted as the specific absorbance A/t , where A is the absorbance ($\log_{10} I_0/I$), uncorrected for reflection or scattering losses, and t is the sample thickness in cm. A single nonpolarized curve was run by N. A. Kuebler (Bell Labs.) on a McPherson 1 m scanning monochromator out to 7 eV. Curve fitting was performed on a DuPont 310 curve resolver, which was used to sum five simultaneous Gaussian components, each with adjustable peak position, height, and width.

Semi-quantitative and quantitative emission spectrochemical analyses were performed on a number of the specimens. The values for Fe, Al, and any other elements present above the 0.000X % level are included in Table II. EPR data were obtained on crystal 542-3 (Nassau and Prescott, 1975).

TABLE I. *Irradiation colors and color-change temperatures of quartz of known origin, all originally colorless*

<i>Locality</i> †	<i>Color Change Temp. (°C)*</i>	
	<i>Smoky to G-Y or Colorless</i>	<i>G-Y to Colorless</i>
<i>A. Smoky Only:</i>		
Pencil Bluff, Ariz.; Morro Velho, Brazil	160 – 180	—
Whitehaven, Pa.; Fords, N. Y.; Middleville, N. Y.; Alamance, Randolph, and Montgomery Counties, N. C.; Hot Springs, Ark.; Dunlap, N. M.; Lannett, Alabama; Panesquira, Portugal; Keystone, S. D.; Madwaska, Ontario, Armstrong, B. C.; Brazil	240 – 300	—
Georgetown, Me.; Greely, Ontario; Dolni Bory, Czechoslovakia; Brazil	320 – 380	—
<i>B. Greenish-Yellow Only:</i>		
Govea, Brazil; Kunkeltown, Pa.	—	200 – 260
<i>C. Smoky Followed by Greenish-Yellow:</i>		
Rio Grande du Sol, Brazil	160	240
Hot Springs, Ark.; Lagrange, Georgia; Haddam, Conn.; Minas Gerais, Brazil; Petaca, N. M.; Crystal Peak, Cal.	240 – 260	260 – 320
Haddam, Conn.; Topsham, Maine; Mendez de Pimental, Brazil; Minas Gerais, Brazil	240 – 260	340 – 380
<i>D. No Irradiation Color:</i>		
Goiaz, Brazil; Minas Gerais, Brazil; Mt. Ida, Ark.; Auburn, Maine; Dougway, Ill.; Alamance County, N. C.	—	—
<i>E. Synthetic Crystals:</i>		
	140 – 340	140 – 380

† Specimens involving blue, blue-green, and green colors are not included in this table.

* G-Y indicates greenish-yellow; color changes were observed with 20° temperature increments with two to four hours at each temperature.

Results

Several types of behavior were observed on irradiating and then heating colorless quartz crystals. Group A of Table I remained smoky until the temperature was reached when they turned colorless; Group C passed through the G-Y color; some showed no smoky color on irradiation, being either colorless (Group D) or G-Y (Group B); all ultimately became colorless. Some synthetic quartz fell into each of Groups A to D, as did some of the massive vein and pegmatite core quartz. Temperature ranges are summarized in Table I.

The smoky coloration can obscure the G-Y color, which means that Group A in Table I could still have G-Y present, with the G-Y merely bleaching at a lower temperature than the smoky. An examination of our absorption spectra could not definitely establish the presence or absence of G-Y in these samples, since we were limited to 5.6 eV in the ultraviolet.

TABLE II. Colors, temperatures, and chemical analyses for some quartz crystals

Designation	Origin	Colours & Temps ($^{\circ}$ C)	Wt. % Al	Wt. % Fe	Other
A: Samples involving A_1, A_2, A_3 ; blue to green:					
X477-3	Synthetic	S/260/B/280/C	0.006	0.0044	ϕ
X536-17BG	Synthetic	S/240/BG/300/C	0.010	0.0015	*†
X536-17S		S/300/C	0.011	0.0024	*
X542-3	Synthetic	S/260/B/320/C	0.011	0.065	*ϕ
4174	Synthetic	S/160/G/360/C	—	—	—
8175	Hot Springs, Ark.	S/280/C	0.002	0.002	—
8574	Morro Velho, Brazil	S/260/C	0.002	0.07	—
B: Samples involving G-Y without smoky:					
8174	Kunkeltown, Pa.	G-Y/200/C	0.009	0.00X	*†
8274	Govea, Brazil	G-Y/260/C	0.020	0.00X	*†
53074	Synthetic	G-Y/140/C	0.003	0.003	*ϕ
X51-17	Synthetic	G-Y/140/C	0.001	0.006	†ϕ
X56-11	Synthetic	G-Y/140/C	0.002	<0.001	ϕ
C: Samples involving G-Y with smoky:					
B3919	Minas Gerais, Brazil	S/260/G-Y/300/C	0.003	0.0002	—
6374	Natural	S/240/G-Y/260/C	0.007	0.003	*†
7401	Natural	S/200/G-Y/240/C	0.014	0.013	*†
8374	Mendez de Pimental, Brazil	S/260/G-Y/360/C	0.20	0.00X	—
8474	Rio Grande Du Sol, Brazil	S/160/G-Y/240/C	0.010	0.00X	—
109570	Minas Gerais, Brazil	S/240/G-Y/320/C	0.035	0.027	*†ϕ
9101G-Y	Natural	S/-/G-Y/-/C	0.0X	0.0X	—
9101S		S/-/C	0.0X	0.00X	—
9102G-Y	Natural	S/-/G-Y/-/C	0.0X	0.0X	—
9102S		S/-/C	0.00X	0.00X	—
9103G-Y	Natural	S/-/G-Y/-/C	0.01	0.000X	—
9103S		S/-/C	0.00X	0.000X	—

All other elements detected in emission spectrochemical analysis were 0.000X% or less except: *Ca 0.00X%; † Li 0.00X low%; and ϕ Na 0.00X%.

Colors are abbreviated as: S smoky; G green; B blue; G-Y greenish-yellow; C colorless. Transition Temperatures refer to 2 to 4 hours at 20 $^{\circ}$ C heating increments.

The statement of Lehmann and Bambauer (1973) that the G-Y coloration is less stable to heat than smoky quartz appears to have been based on one specimen and can be seen to have no general validity. Our previous statement of the reverse (Nassau and Prescott, 1975) has also proved invalid on the testing of additional specimens.

Many natural quartz specimens labeled 'Brazil', or not otherwise identified as to origin fell into each of the four groupings of Table I. Some natural smoky quartz fell into Group A, and some into Group C. Many samples showed banding and sectioning of the colors and more than one type of behavior in different parts of the same crystal.

Not included in Table I are four types of specimens:

The amethyst—'greened amethyst' partly heated specimen from Bahia, Brazil (Smithsonian No. 3297); checked by irradiation and heating experiments, it proved to be typical material of the kind usually attributed to the Rio Prado region of Minas Gerais (Rose and Lietz, 1954; Cohen, 1956), which is close to the border of Bahia.

The unique Dana 44678A and B specimens, which were distinct from the other greens and also from 'greened amethyst' and will be described elsewhere (Nassau *et al.*, to be published).

The B3919 and 109570 samples described below, which were the only naturally occurring G-Y quartzes we have been able to locate.

And the majority of synthetic quartz crystals, which showed a series of colors ranging from blue to green to brown, which could be explained by various combinations of blue (A_1 and A_2) and smoky (A_3) absorptions; blue by itself was observed in crystals from four growth runs and the study of one of these permitted the clear isolation of the A_1 and A_2 spectrum, which then could be recognized as a component of the majority of both natural and synthetic specimens.

Blue quartz and the A_1 , A_2 , and B bands. Several specimens from four experimental growth runs performed at Western Electric, Merrimack Valley Works, became a dark smoky color on irradiation but turned blue when subsequently heated at 160 to 280 °C; at 300 to 360 °C they again became colorless. The darkest blue color in a 0.5 cm thick slab of sample X542-3 corresponds to no. 180, very light blue, on the ISCC-NBS scale (Kelly and Judd, 1965).

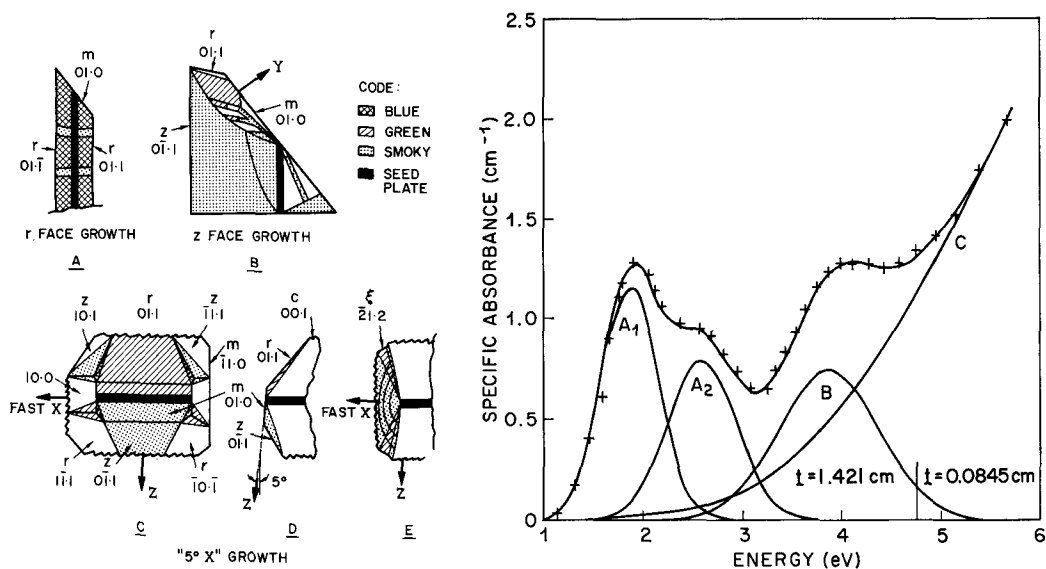
The growth runs had been performed in silver-lined autoclaves from 1.0 *N* NaOH. The runs X538-3 and X542-3 contained 0.03 *M* FeSO₄ and added silicon metal (equivalent to 0.22 *N* and 0.11 *N* respectively) to maintain reducing conditions; X477-3 and X511-5 contained neither Fe nor Si. Lithium was not added to these runs.

The deepest blue color was observed and all subsequent work was performed on a major rhombohedron (*r*-face) seed crystal grown in run X542-3 at 21 mils per day. This seed contained some low-angle grain boundaries, as shown by the fact that the segments of the grown *r*-faces were not coplanar. The misorientation regions presumably involved growth directions other than *r*-face growth and yielded some smoky coloration that did not bleach to blue on heating. This behavior is illustrated in fig. 1A and in color at the lower left in fig. 9 of Nassau, 1974.

Spectrochemical analysis of the deep blue region showed 0.065 % Fe, 0.011 % Al, 0.00X % Ca and Na; and 0.000X Ag, Cr, Cu, Ga, Li, Mg, and Mn. The iron content corresponds to 0.093 % Fe₂O₃, which falls into the amethyst range (Fron del, 1962). This Fe presumably was not substitutional, since no amethyst color was observed either visually or in the spectrum after irradiation (Barry *et al.*, 1965; Chentsova *et al.*, 1966), nor were the citrine or 'greened amethyst' (Rose and Lietz, 1954) colors or spectra obtained after heating. The iron content is not involved in the blue spectral features, since sample X536-17, which had only 0.0015 % Fe, also showed the same features, as do specimens with an iron content of less than 0.0002 % and, indeed, as does essentially all smoky quartz. The possibility exists that the reducing

conditions of X538-3 and X542-3, or the high purity conditions of X477-3, permitted the smoky-causing absorption to bleach at a lower temperature than the blue-causing absorption.

The detailed polarized absorption spectra and EPR data on X542-3 have been given by Nassau and Prescott (1975). The resolution of the π (extraordinary ray) polarization spectrum into Gaussian components is shown in fig. 2. The A_1 and A_2 components have been designated after the similarly placed features previously associated with smoky quartz. The B component has been known only in fused silica as an irradiation-induced band associated with aluminum and alkali ion impurities (Lell, 1962; Mitchell and Paige, 1964). It shows very clearly in all our spectra. The C band appears to be the usual absorption with a peak at 6.05 eV (Mitchell and Paige, 1964).



FIGS. 1 and 2: FIG. 1 (left). Color distribution observed in some synthetic quartz crystals after γ -irradiation and heating: A—crystal X542-3; B—crystal LC3094-14; crystal X43-20 at crystal end C and longitudinal cross-section D; E—crystal LC2283-12, transverse cross-section. Crystal surfaces drawn with wavy lines are not crystallographic faces but vicinal development type irregular surfaces. Miller-Bravais indices follow the system given by Heising (1946) with $+X \equiv a_1 \equiv 2\bar{1}10$; lefthanded. FIG. 2 (right). The π spectrum of synthetic quartz crystal X542-3 turned smoky by γ -irradiation and heated to 280 °C to become blue: crosses—experimental values; lines—Gaussian components and their summation.

The σ (ordinary ray) polarized spectra resolved into the same Gaussian components as the π spectra but with less clarity.

The A_1 , A_2 , and B peaks are located at 1.85 eV, 2.55 eV, and 3.95 eV, respectively. These values are somewhat displaced from the positions previously reported, namely 1.94 to 2.00 eV for A_1 and 2.56 to 2.70 eV for A_2 , (Lell *et al.*, 1966). This was to be expected since the older values were generally taken without curve-fitting and in the presence of the unsuspected A_3 and B bands. Our band positions were consistently within ± 0.1 eV. The half-widths (width at half the peak height) are 0.7 eV for A_1 , 0.8 eV for A_2 , and 1.2 eV for B.

Smoky quartz and the A_3 absorption band. When re-irradiated, the blue X542-3 quartz specimen again turned smoky, fig. 3. The intensity of the smoky coloration correlated (Nassau and Prescott, 1975) with the new A_3 absorption band as well as with the hexet substitutional aluminum-hole EPR center (Griffiths *et al.*, 1954; O'Brien, 1955; Mackey, 1963; Schnadt and

Schneider, 1970). Some properties of this center have been reported by Shternberg *et al.* (1970) and Schnadt and Räuber (1971).

All the analysed crystals showing the smoky A_3 band contained sufficient aluminum (at least 0.000X % as seen in Table II) to be consistent with this assignment.

The A_3 band occurs at 2.90 eV and has a half-width of 1.5 eV. It can now be positively identified as the origin of the gray to black 'smoky' color in smoky quartz. By itself, A_3 does not give any yellowish, reddish, or greenish tints.

The data of Tables I and II indicate a wide range of bleaching temperatures for the smoky A_3 absorption, from 140 to 380 °C for a two- to four-hour heating period. The bleaching step corresponds to the return of the trapped electron to the color center (i.e. to the hole on an oxygen adjacent to the substitutional aluminum); the variation in temperature thus indicates a range of possible activation energies for the release of this electron. The temperatures listed in Tables I and II correspond to the total loss of color; much color has already been lost well below this temperature in most specimens, indicating more than one trapping site. It is possible that the alkali ions and protons that charge-compensate the aluminum (Lell *et al.*, 1966) may provide these trapping sites. It has been noted by B. W. Sawyer (1974, 1976) that the smoky ('gray') color resulting from slight irradiation correlated well with the aluminum content and he attributes it to aluminum charge compensated with an alkali metal ion.

Greenish yellow (G-Y) quartz. Some natural and synthetic quartz turns a G-Y color on irradiation (Lehmann, 1971; about 2 % of the samples we tested fell into Group B of Table I). Much natural quartz gives the G-Y color after heating to bleach the smoky irradiation color, which usually hides it (Samoilovich *et al.*, 1968; about a quarter of the samples we tested fell into Group C of Table I).

This color has been variously termed 'yellow' (Sawyer, 1974, 1976), 'yellow' and 'honey' (Lehmann, 1971; Lehmann and Bambauer, 1973), and 'greenish yellow' as well as 'radiation-produced citrine' (Samoilovich *et al.*, 1968). To avoid confusion with the allochromatically iron-caused citrine color and to provide a unique and appropriate designation, 'G-Y quartz' is used here. The color in a 1-cm thick piece corresponds to no. 101 light greenish yellow, on the ISCC-NBS scale, which converts to 9.8 Y 8.9/7.0 in the Munsell notation (Kelly and Judd, 1965).

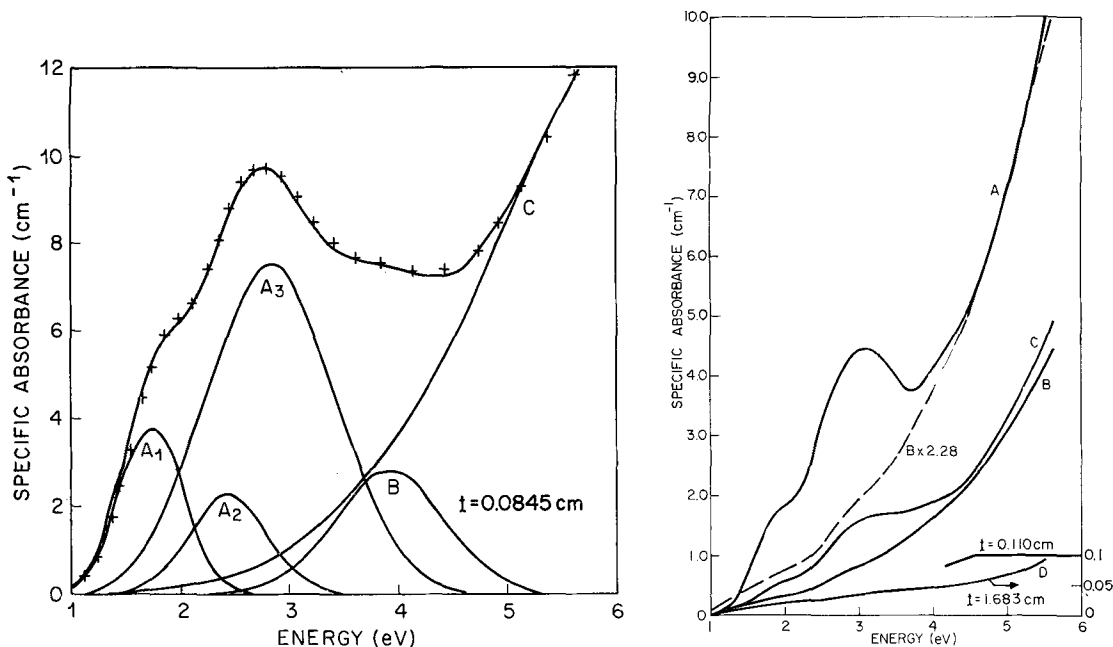
Three samples were studied in detail: 6374 was a colorless natural crystal of unknown origin; B3919 was one of the two naturally occurring G-Y quartzes we have been able to locate; 53074, a synthetic colorless crystal, also gave a G-Y color on irradiation but did not acquire any A_1 , A_2 , or A_3 absorptions and therefore did not require heating to develop G-Y. Analyses for these specimens are included in Table II.

In fig. 4 are given the π spectra of 6374. Irradiation to saturation (15 megarads) gave Curve A and heating to 250 °C gave the G-Y stage, Curve B. Irradiation with 0.17 megarads gave the smoky yellow of Curve C, and heating to above 260 °C returned the crystal to colorless.

The color difference between Curves B and C is shown in fig. 5a together with its Gaussian decomposition. A more detailed view is obtained by subtracting from Curve A of fig. 4 the absorption values corresponding to Curve B multiplied by 2.28 to produce coincidence in the 5 eV region. This difference curve, fig. 5b, shows that A_1 , A_2 , and A_3 fully account for the excess of the 'smoky' state over the G-Y state of curve B of fig. 4, the dominant contribution arising from the A_3 absorption band.

The G-Y color originates from the tail of an intense absorption band extending down through the visible region. This may belong to one of the C, D, or E bands (occurring at 5.7, 7.15, and 7.6 eV), or to other bands at 7.4, 7.8, and 8.0 eV described by Mitchell and Paige (1956) and Nelson and Weeks (1961). The curves of fig. 6 showing the unpolarized spectrum

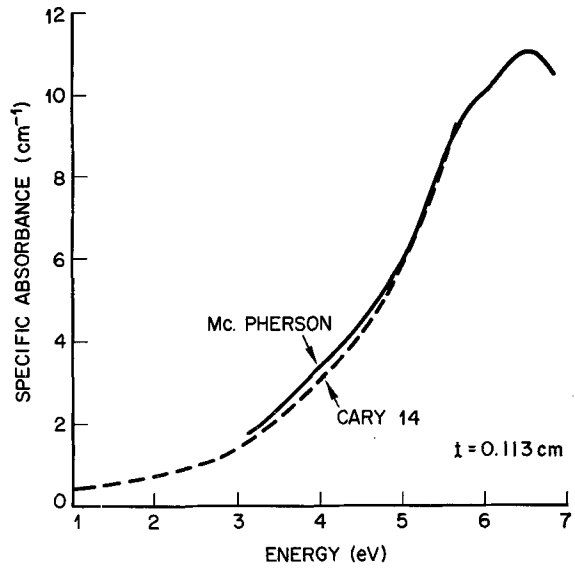
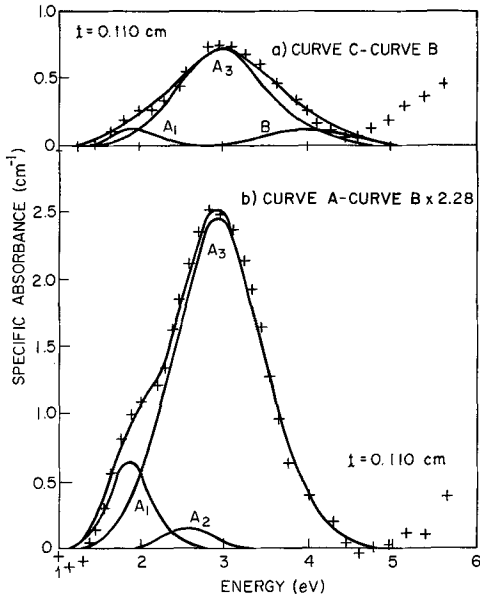
of the sample of fig. 4 extended into the UV to 7 eV by N. A. Kuebler give indications of a peak at $6\frac{1}{2}$ eV, a shoulder at 6 eV, and the possibility of a component near 4 eV, any of which could provide the tail causing the G-Y. Preliminary vacuum ultraviolet data run by C. E. Jones of Lehigh University indicate large differences in the absorptions in this region among some of the samples of this study.



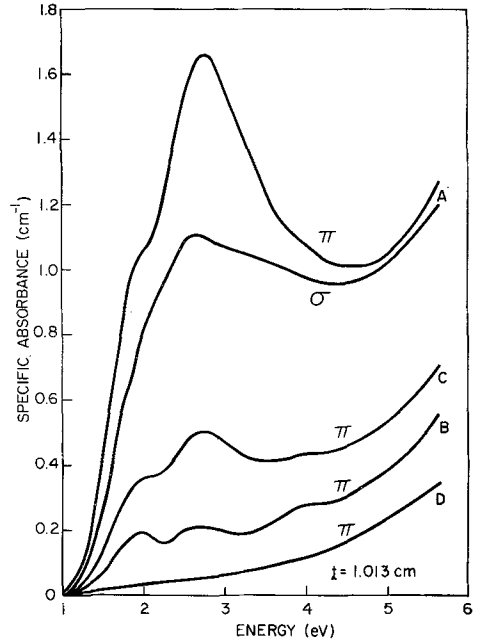
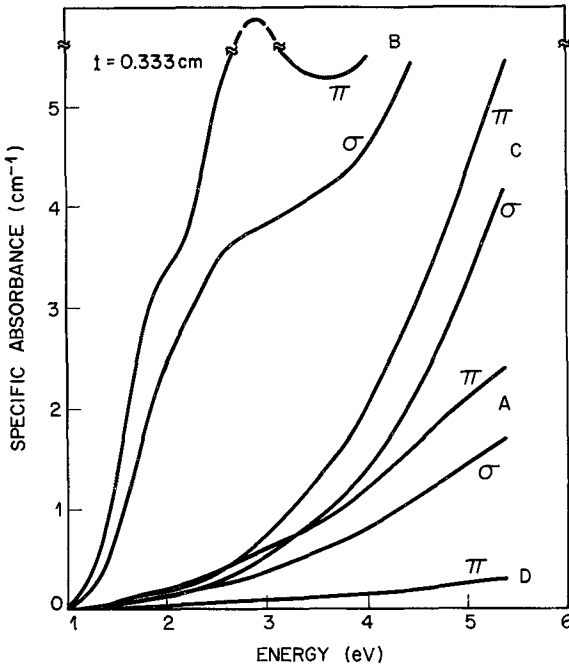
FIGS. 3 and 4: FIG. 3 (left). The Gaussian composition of the π spectrum of smoky quartz crystal X542-3 after saturation with γ -rays. FIG. 4 (right). The π spectra of a natural quartz crystal no. 6374 irradiated to saturation (A—smoky color), heated to 240 °C (B—G-Y color), re-irradiated for 15 min (C—smoky G-Y), and heated to 500 °C (D—colorless). Dashed line is curve B multiplied by 2.28 to coincide with curve A in the 5 eV region.

The polarized spectra of the natural quartz B3919 are shown in fig. 7 in the G-Y as-received state at A, smoky after irradiation to saturation at B, again G-Y after heating to 260 °C at C, and in the colorless form after heating to over 300 °C at D. The as-received spectra (fig. 7A) are similar to those of the fully developed G-Y spectra (fig. 7C) except that somewhat more bleaching had taken place in A. It can be suggested that this specimen had been smoky at one time and had subsequently been heated during its geological history, possibly to a much lower temperature than 260 °C for an extended period of time. The similarity to specimen 6374 (fig. 4B) is obvious and difference curves also gave results similar to those of fig. 5.

The other naturally occurring G-Y crystal, 109570, a large 9-cm termination, behaved quite similarly to B3919 (Table II). A check of commercial jewelry containing smoky, citrine, or 'topaz' quartz faceted stones showed an occasional specimen that was clearly greenish yellow rather than the more usual citrine or smoky color. Natural specimens of G-Y quartz usually have a low color saturation and then show only a pale yellow color. The designation G-Y is, however, still desirable in that it distinguishes the material from Fe-produced citrine (which has a distinctly different shade of yellow even at low concentration) and from smoky quartz (which is grayish brown and not yellow at low concentrations).



FIGS. 5 and 6: FIG. 5 (left). Difference curves and their Gaussian decomposition for the spectra of fig. 4. FIG. 6 (right). Extension of the unpolarized spectrum of no. 6374 in the G-Y state (equivalent to fig. 4) to 7 eV.



FIGS. 7 and 8: FIG. 7 (left). Polarized spectra of a natural G-Y quartz crystal B3919 in the as-received form (A—G-Y color), irradiated to saturation (B—smoky), heated to 260 °C (C—G-Y color), and heated to 500 °C (D—colorless). FIG. 8 (right). Polarized spectra of a synthetic quartz crystal X536-17 irradiated to saturation (A—smoky), heated to 240 °C (B—green), re-irradiated for 15 mins (C—smoky green), and heated to 300 °C (D—colorless).

The synthetic crystal 53074, and two other similarly behaving specimens X51-17 and X56-11, were grown by Western Electric. These were rapid 'ageing' growth runs using 0.5 *M* NaOH and 0.05 *M* Li₂CO₃. These three samples gave a G-Y color on irradiation without showing any smoky features and became colorless again on heating to 140 °C. The spectra were similar to curves C of fig. 7 and analytical data are included in Table II.

A number of natural quartz crystals after being irradiated and heated showed separate zones of G-Y and smoky color. Paired analyses are given in Table II for three of these samples (9101, 9102, and 9103); these data are inconclusive, the cause for the differences apparently being more subtle than merely the Fe and Al concentrations.

The temperature range for the bleaching of the G-Y color (140 to 380° in Table I) is identical with that for the smoky color. This suggests that the G-Y color centers are also hole centers, different from the smoky centers, but with the displaced electrons trapped at the same types of traps. There would then be a need to explain the data of Sections C of Tables I and II showing that a higher temperature is needed to bleach the G-Y in some of those specimens where both G-Y and smoky are present together. It is possible that preferential clustering can occur in some specimens depending on the growth conditions, with the lower-temperature-releasing traps being adjacent to the smoky absorption-causing centers. If this is so, then the diffusion of alkalis (Mackey, 1963) would be expected to change the bleaching temperature. B. Sawyer (1974, 1976) has noted that the intensity of the G-Y coloration ('yellow') resulting from slight irradiation correlates well with the aluminum content and attributed it to aluminum charge compensated with hydrogen ions.

Blue-green and green quartz related to the blue color. The majority of synthetic quartz specimens tested showed some blue-green or green color on irradiation followed by heating. The curves of fig. 8 show such a specimen, X536-17. The resemblance between fig. 8B and fig. 4 of Nassau and Prescott (1975) is striking. Gaussian curve analysis shows that these curves can be fully explained by mixtures of A₁, A₂, A₃, B, and C.

The conclusion is that the bulk of the smoky coloration in X536-17 bleached on heating to 240 °C, but the residual absorptions from bands A₁, A₂, and A₃ left at this point bleached at the same rate. Thus the blue color due to A₁ and A₂ by themselves cannot be obtained in such a specimen.

The distribution of blue-green to green colors is shown in fig. 1B to E. This shows the stage when almost all the smoky coloration has been bleached by heating to about 260 °C (Section A of Table II). The blue-green and green generally are observed in '5°X' grown quartz (1.0 *M* NaOH, 0.025 *M* Li₂CO₃; Ballman *et al.*, 1966) on the major rhombohedral faces (type *r*), while growth on the minor rhombohedral face (type *z*) retains some smoky color as shown in figs. 1C and D. Figs. 1B to E show the rather complicated color sectoring that can occur. Detailed study will be needed for the exact interpretation of color distributions such as these.

Some irradiated synthetic crystals show even more extreme variation in behavior on heating in different parts of the crystal; the most varied sequences were the following (using the convention of Table II):

Sample X507-15:

Major rhomb growth S/220/B/280/C
 Minor rhomb growth S/140/C
 5° off (0001) growth S/140/G-Y/380/C

Sample X538-3:

Major rhomb growth S/260/G/280/G-Y/380/C
 Minor rhomb growth S/280/C.

It will be noted that in X538-3 the G-Y color developed after green, so that here the green may be due to a blue/G-Y combination rather than the more frequently observed blue-brown combination, which can also produce a green.

The temperature extremes for color changes among the synthetic crystals as compared to natural crystals are given in Table III.

TABLE III. *Temperature ranges observed for various color changes in synthetic and natural quartz*

Color Change*	Synthetic	Natural	Color Change*	Synthetic	Natural
S to G, BG, or B	160 – 280°C	–	S to C	140 – 340°C	160 – 380°C
S to G-Y	140 – 300°C	160 – 260°C	G, BG, or B to C	280 – 360°C	–
G or BG to G-Y	280°C	–	G-Y to C	140 – 380°C	200 – 380°C

*S smoky; G green; B blue; BG blue-green; G-Y greenish-yellow; C colorless

The 'anomalous pleochroism' in synthetic quartz of Tsinober (1962) and Tsinober *et al.* (1967) is also being examined and appears to fall within the A₁, A₂, A₃, B, C absorption band framework and will be described later (Nassau *et al.*, to be published), as will be the unique green Dana 44678 specimens.

Conclusions

This work provides some partial explanations for the irradiation colors in quartz, in particular for the wide range of smoky colors, originating in mixtures of smoky (A₃), blue (A₁ and A₂), and greenish-yellow (G-Y) absorption bands. In addition many new questions are raised. Among these are the identification of the origin of the blue A₁ and A₂ and the G-Y absorptions. The results of a number of previous investigations, which studied, for example, the kinetics of bleaching of the A bands and their relationship to other absorption features, now become uncertain, since it is not clear if the A₁ and A₂ bands or the A₃ band or all three were in fact being studied. An intriguing problem is the nature of the various electron traps and the distribution of trapped electrons, leading to the various bleaching temperatures in different crystals as well as different color zoning within one crystal.

Acknowledgements. We wish to acknowledge helpful discussions with R. L. Barns, C. R. Kurkjian, E. D. Kolb, N. A. Kuebler, G. E. Peterson, and D. L. Wood, all of the Bell Labs., and F. J. Feigl and C. E. Jones of Lehigh University. We would like to thank R. L. Barns for the polariscope result, G. E. Peterson for the EPR measurements, N. A. Kuebler for the far-UV spectrum, and E. D. Kolb for the etching result. We are grateful to J. S. White and P. Dunn of the Smithsonian Institution, C. M. Curtis of Chatanooga, Tenn., C. Frondel and D. K. Cook of Harvard University, H. Winchell of Yale University, and many others for many of the specimens that made this study more meaningful.

REFERENCES

- Ballman (A. A.), Laudise (R. A.), and Rudd (D. W.), 1966. *Appl. Phys. Lett* **8**, 53-4.
 Barry (T. I.), McNamara (P.), and Moore (W. J.), 1965. *J. Chem. Phys.* **42**, 2599-2606.
 Chentsova (L. G.), Tsinober (L. I.), and Samoilovich (M. I.), 1966. *Soviet Phys.—Crystallogr.* **11**, 219-23 (transl. of *Kristallografiya*, **11**, 236-44, 1966).
 Cohen (A. J.), 1956. *Am. Mineral.* **41**, 874-91.
 ——— 1975. *Ibid.* **60**, 338-9.
 Frondel (C.), 1962. *The System of Mineralogy* (John Wiley and Sons, Inc., New York), 7th edn., 3, 137-42 and 171-86.
 Griffiths (J. H. E.), Owen (J.), and Ward (I. M.), 1954. *Nature*, **173**, 439-40.
 Halperin (A.) and Ralph (J. E.), 1963. *J. Chem. Phys.* **39**, 63-73.
 Heising (R. A.), 1946. *Quartz Crystals for Electrical Circuits* (D. Van Nostrand Co., Inc., New York), 104 and 106.

- Kelly (K. L.) and Judd (D. B.), 1965. The ISCC-NBS Method of Designating Color and a Dictionary of Color Names (including the supplement: ISCC-NBS Color Name Charts Illustrated with Centroid Colors). *Circular 533, 2nd edn.* Natl. Bur. Stand. U.S. Govt. Printing Office, Washington, D.C.
- Laudise (R. A.), 1962. Hydrothermal Synthesis of Single Crystals. In F. A. Cotton, Ed., *Progress in Inorganic Chemistry*, **3**, 1-47 (Interscience Publishers, New York).
- Lehmann (G.), 1971. *Phys. stat. solids*, **B48**, K65-7.
 — 1975. *Am. Mineral.* **60**, 335-7.
 — and Bambauer (H. U.), 1973. *Angew. Chem. Int. Ed.* **12**, 283-91.
- Lell (E.), 1962. Radiation Effects in Doped Fused Silica. *Phys. and Chem. Glasses*, **3**, 84-94.
 — Kreidl (N. J.), and Heusler (J. R.), 1966. Radiation Effects in Quartz, Silica and Glasses. In J. E. Burke, Ed. *Prog. Ceram. Sci.* **4**, 1-93 (Pergamon Press, New York).
- Mackey (J. H., Jr.), 1963. *J. Chem. Phys.* **39**, 74-83.
- Mitchell (E. W. J.) and Paige (E. G. S.), 1956. *Phil. Mag.* **1**, 1085-1115.
 — — 1964. *Proc. Phys. Soc.* **67B**, 262-4.
- Nassau (K.), 1974. *Lapidary Journal*, **28**, 1064-74, 1084.
 — and Prescott (B. E.), 1975. *Phys. stat. solids*, **A29**, 659-63.
- Nelson (C. M.) and Weeks (R. A.), 1961. *J. Appl. Phys.* **32**, 883-6.
- O'Brien (M. C. M.), 1955. *Proc. R. Soc. A* **231**, 404-14.
- Rose (H.) and Lietz (J.), 1954. *Naturwiss.* **41**, 448.
- Samoilovich (M. I.), Tsinober (L. I.), Khadzhi (V. E.), and Lelekova (M. V.), 1968. *Soviet Phys.—Crystallogr.* **13**, 734-6 (transl. of *Kristallografiya*, **13**, 850-3, 1968).
- Sawyer (B.), U.S. Patent 3,837,826, 24 September 1974.
 — U.S. Patent 3,936,188, 3 February 1976.
- Schnadt (R.) and Rauber (A.), 1971. *Solid State Commun.* **9**, 159-61.
 — and Schneider (J.), 1970. *Phys. kondens. Mater.* **11**, 19-42.
- Shternberg (A. A.), Gordienko (L. A.), and Tsinober (L. I.), 1970. *Soviet Phys.—Crystallogr.* **14**, 728-32 (transl. of *Kristallografiya*, **14**, 845-51, 1969).
- Tsinober (L. I.), 1962. *Soviet Phys.—Crystallogr.* **7**, 113-14 (transl. of *Kristallografiya*, **7**, 138-9, 1962).
 — Samoilovich (M. I.), Gordienko (L. A.), and Chentsova (L. G.), 1967. *Soviet Phys.—Crystallogr.* **12**, 53-6 (transl. of *Kristallografiya*, **12**, 65-9, 1967).

[Manuscript received 10 May 1976; revised 6 September 1976]

Errata: Table I, section A, line 6: For Madwaska, Ontario, read Madwaska, Ontario;
 Table II, sample 8374: For Mendez de Pimental, read Mendez de Pimental,