A TRANSMISSION ELECTRON MICROSCOPE STUDY OF AMETHYST AND CITRINE

By A. C. McLaren* and P. P. Phakey*

[*Manuscript received November* 10, 1964]

Summary

Thin crystals of amethyst and citrine were examined by transmission electron microscopy. It was found that all crystals became damaged during observation. The diffraction contrast from the damage centres indicated that these were small amorphous regions. Electron spin resonance observations of these crystals show that the amorphous regions are associated with Fe^{3+} ions; the damage centres provide, therefore, a measure of the distribution of this impurity in the crystals. Brazil twin boundaries, generally of the order of 1000 Å apart, were observed directly. Radiation damage occurred preferentially at the twin boundaries suggesting that there was a concentration of impurities along them. The relevance of these observations to the optical properties of the crystals is discussed briefly.

I. Introduction

Diffraction contrast electron microscopy has been used extensively over the past 10 years for the direct observation of structural defects in a large range of metals, alloys, and other crystals. The basis of the technique and its application has been described by Thomas (1962). However, apart from the recent work of Evans (1962, 1963) on diamond and bluejohn, and of Fleet and Ribbe (1963) on moonstone, there appears to have been no application of the technique to the study of minerals of gemmological or geological interest.

We are at present undertaking in this laboratory an investigation, by transmission electron microscopy, of a number of such minerals. In the present paper we give the results of the first stage of a study of the two closely related quartz minerals amethyst and citrine.

Amethyst (and to a lesser extent citrine) is used extensively as a semiprecious gemstone and there has been much speculation about its optical properties, in particular its colour and anomalous biaxial character. There is considerable evidence that these properties are intimately associated with the polysynthetic Brazil twinning which appears to be present invariably (Frondel 1962). The structural relationship of the individuals of a Brazil twin is that of reflection across planes of the type $\{11\bar{2}0\}$; that is, across the composition plane the orientation changes from right- to left-handed or vice versa. Brazil twinning can be observed in thick crystals in polarized light because the plane of polarization is rotated in opposite directions in the twinned parts, but it is not observable in thin sections since the amount of optical rotation is too small and there is, of course, no change in the direction of the optic axis across the twin boundaries. It is possible, therefore, to examine Brazil twins by optical microscopy only at low magnifications. However, we have found that

* Department of Physics, Monash University, Clayton, Vic.

Brazil twin boundaries are visible directly by electron diffraction contrast and hence may be studied in detail at high magnification in the electron microscope.

Information about the distribution of impurities in the crystals has been obtained from observations of the electron-radiation damage that takes place during observation in the microscope.

II. Experimental

Thin specimens suitable for transmission electron microscopy were prepared from gem-quality specimens in the following way: small pieces of crystal (about 1 mm in size) were first crushed between two glass microscope slides; after separating the slides a carbon film was deposited on to them in a vacuum evaporator; the carbon film was floated off the slides in water and picked up on standard electron microscope specimen grids. Examination under an optical microscope showed that a large number of crystal fragments adhered to the carbon film. The crystal fragments were then examined in a JEM-6A electron microscope operating at 100 kV. The specimen stage could be tilted $\pm 6°$, allowing the orientation of the specimen relative to the electron beam to be adjusted to obtain optimum diffracting conditions.

III. Results

(*a*) *Amethyst*

It was found that within one minute of commencement of exposure to the beam of the electron microscope all crystals of amethyst became damaged, with the development of black spots. As the irradiation was continued the spots grew large enough to be identified as loops when one reflection was operating. Typical examples are shown in Plate 1(*a*). On continued irradiation the loops grew and eventually coalesced, resulting in the complex appearance shown in Plate 1(*b*). After about 10 min irradiation the contrast began to disappear, as can be seen in Plate 1(*c*). Eventually all contrast disappeared and selected area diffraction showed that the crystal had become amorphous. In some crystals the damage developed in bands similar to those shown in Plate 4, Figure 2.

Many of the crystals examined showed sets of parallel straight lines which could be tilted in and out of contrast. The spacing between the lines was of the order of 1000 Å. Although the damage generally occurred throughout the crystal it took place more rapidly along the lines, which thus became decorated with damage centres. In Plate 2, in addition to the damage-decorated straight lines at A, typical thickness fringes due to plane defects inclined to the surface of the crystal can be seen at B. These also show evidence of decoration. In addition, they taper towards the edge of the crystal, as would be expected in a crystal of wedge-shaped cross section. The colour was never distributed uniformly throughout the crystals and, in general, it was found that the line and plane defects were more common in the deeper coloured regions. The irregularly shaped decorated line at C in Plate 2 is, possibly, a dislocation. On continued irradiation in the electron beam it was observed that the regions of the crystal along the straight lines were the first to become amorphous. This is shown clearly in Plate 3.

The colour of crystals which had been annealed in air at temperatures up to 540°C for about 10 hr changed to the yellow of citrine, but in the electron microscope they could not be distinguished from unheated crystals.

(*b*) *Citrine*

Crystals of natural citrine behaved very similarly to amethyst. Good examples of inclined tapering plane defects are shown in Plate 4, Figure 1. Although this photograph was taken within about a quarter of a minute of the crystal being exposed to the electron beam, it will be seen that damage has occurred throughout the crystal but preferentially at the plane defects. Banding of the damage centres, independently of line or plane defects, was also observed (Plate 4, Fig. 2).

Annealing in air at about 500°C affected neither the colour of these crystals nor their behaviour in the electron microscope.

(*c*) *Other Quartz Minerals*

A preliminary examination was also made of samples of synthetic quartz of unknown purity and naturally occurring clear, smoky, and rose quartz. These minerals all behaved in a similar way. However, unlike amethyst and citrine, they exhibited no line or plane defects, and the degree of damage in the electron beam varied markedly from sample to sample and within any particular crystal fragment.

Generally, the density of damage centres was significantly lower than in amethyst and citrine, thus the loops could grow much larger before coalescing. An example of this in clear natural quartz is shown in Plate 4, Figure 3, which was taken about 15 min after the beginning of observation. It will be seen also that the contrast from these large damage centres is not a single loop but consists of a number of lobes placed approximately symmetrically about a line whose direction is common to all the loops. Selected area diffraction of a number of similar crystals showed that the line of symmetry was perpendicular to the reciprocal lattice vector $\mathbf{g}$ corresponding to the operating reflection. On prolonged irradiation the contrast disappeared, the crystals becoming amorphous.

Fracture marks produced during specimen preparation were observed in all the minerals examined, and particularly good examples can be seen in Plate 4, Figure 1. It will be seen that there are no dislocations indicating plastic deformation associated with the fracture marks, as have been observed in zircon by Bursill and McLaren (1965).

IV. Discussion

(*a*) *Nature of the Radiation Damage*

It has been shown that all the quartz crystals examined became amorphous on prolonged irradiation. The transformation to the amorphous state involves a volume change of about +18%. The damage centres which grow into loops during observation in the electron microscope are the precursors of the amorphous state. In clear natural quartz the contrast from the large damage centres is remarkably similar to the diffraction contrast due to strain around a spherical inclusion, which

has been discussed in detail by Ashby and Brown (1963*a*). Attention is drawn particularly to Figure 10 of their paper. In amethyst and citrine, owing to the high density of damage centres, the loops generally coalesce before growing large enough to exhibit the characteristic diffraction contrast due to strain around a spherical inclusion. Subsequent work by us (paper in preparation) has shown that the density of damage centres is significantly lower in amethyst which has been annealed at 700°C. In such crystals large damage centres showing the characteristic strain contrast are observed. However, it is clear from Plates 1 and 3 that the loops are associated with elastic strain. Hence it is suggested that the loops are due to small amorphous regions exerting a strain on the surrounding crystalline matrix.

As a check on this interpretation, the damage centres during their early stages were imaged by structure factor contrast. The tilt was adjusted to give sharp thickness extinction contours near the edge of the crystal. In the region illustrated in Plate 4, Figure 4, the deviation from the Bragg angle was small ($s \simeq 0$) and it will be seen that the contrast from the damage centres reverses across the thickness extinction contours. On the thin side of the contour (that is, towards the edge of the crystal) the damage centres are white, while on the thick side of the contour the damage centres are black; that is, the effective thickness of the crystal is reduced by a damage centre. Ashby and Brown (1963*b*) have pointed out that if a crystal of thickness t contains an inclusion of thickness Δt then the inclusion will increase the effective thickness of the crystal by an amount

$$\Delta t\{(\xi_g^i)^{-1}-(\xi_g)^{-1}\},$$

where ξ_g^i and ξ_g are the extinction distances of the inclusion and the matrix respectively. The extinction distance is defined by

$$\xi_g = (\pi V/F\lambda)\cos\theta_g,$$

where V is the volume of the unit cell, θ_g is the Bragg angle corresponding to the reflection $\mathbf{g}$, λ is the wavelength of the electrons, and F is the structure factor. Although the expression for the increase in effective thickness of the crystal assumes that the structures of the inclusion and the matrix are identical, we have applied it to the present case of an inclusion of amorphous silica in quartz. Near $s = 0$ the structure factor for the matrix will be very large compared with the structure factor of the amorphous inclusion. It follows that $\xi_g^i \gg \xi_g$ and, therefore, the amorphous inclusion will decrease the effective thickness of the crystal, as is observed.

The mechanism by which the transformation to the amorphous state takes place is not completely understood. The rapid movement of bend extinction contours on focusing and defocusing the illumination indicates that the crystals become heated in the beam, but it is difficult to estimate the temperature reached. However, for a small crystal supported on a thin carbon film in vacuum a temperature rise of several hundred degrees Celsius is likely. Although all diffraction patterns could be indexed satisfactorily, assuming the crystals were α-quartz, we cannot be sure that the crystals have not been heated above the $\alpha \rightarrow \beta$ transformation at 573°C. The structure change at this transformation is so small that it is impossible to distinguish between the two structures with the resolution attainable when using the

electron microscope for selected area diffraction. However, the temperature reached by the crystal cannot have exceeded 700°C, where both amethyst and citrine turn milky owing to the development of bubbles about 500 Å in diameter (paper in preparation).

Since crystals which were heated to 540°C outside the microscope were undamaged when examined subsequently, it must be concluded that the damage is in some way associated with the direct interaction of the electron beam with the specimen. The process may, however, be accelerated by the elevated temperatures. It is unlikely that the damage is due to bombardment by heavy negative ions produced in the electron gun, because the damage ceased to occur when the electron beam was deflected away from the specimen by the magnetic field of a small magnet outside the microscope. If the damage had been due to negative ions then it would have been expected to continue, since these ions would be deflected less than the electrons by the field of the external magnet.

It has been seen that amethyst and citrine behave similarly in the electron beam, but differently from the other quartz minerals examined. Analyses quoted by Frondel (1962) indicate that iron is the major impurity in amethyst and citrine, but that it is a relatively minor impurity and may even be absent in the other minerals. This suggests that the difference in the behaviour of amethyst and citrine compared with other quartz minerals is associated with the difference in concentration of this impurity.

Electron spin resonance (ESR) studies of these minerals by Hutton (1964) have shown that three sharp resonance lines are common to both amethyst and citrine and that they are associated with Fe^{3+} ions. In natural and annealed citrine, and in amethyst whose colour has been changed to that of citrine by annealing, there is an additional broad line which Hutton and Troup (personal communication) interpret as being due to unpaired electrons associated with Fe^{3+} ions in amorphous surroundings. This suggests that the yellow colour is connected intimately with these impurity ions. Presumably it is these small amorphous regions that grow during observation in the electron microscope and give rise subsequently to the diffraction contrast strain loops. Since the crystals are heated probably to about 500°C in the beam, initially unannealed amethyst is expected to behave similarly to the annealed crystals.

Macroscopic observations show that in annealed amethyst the distribution of the yellow colour is the same as that of the original amethyst colour. The electron microscope and ESR observations suggest, therefore, that the detailed distribution of the colour in amethyst and in citrine may be inferred from the distribution of the damage centres.

(*b*) *Nature of the Line and Plane Defects*

From the selected area diffraction patterns it has been found that the parallel lines at A in Plates 2 and 3 are perpendicular to the reciprocal lattice vector of the plane $(10\bar{1}1)$. The presence of the corresponding spot on the diffraction pattern indicated that this plane was, in fact, also perpendicular to the plane of the specimen. It is known (Frondel 1962) from macroscopic and optical microscopic observations that

this plane is one of the set of composition planes of Brazil twinning. Therefore, we interpret these lines as Brazil twin boundaries perpendicular to the plane of the specimen.

The plane defects inclined to the plane of the specimen at B in Plate 2 are seen to be approximately perpendicular to the planes at A. Analysis has shown that Brazil twin composition planes $(\bar{1}101)$ and $(0\bar{1}11)$ are at an angle of 85° 46′ to $(10\bar{1}1)$. The agreement is sufficiently good for us to interpret these plane defects as Brazil twin boundaries also.

In Plate 2 the planes $(\bar{1}101)$ and $(0\bar{1}11)$ are inclined to the normal to the specimen at angles of 21° 10′ and 64° 30′ respectively. Since the spacing of the thickness fringes at each twin boundary is not obviously different the planes of the boundaries must be either all $(\bar{1}101)$ or all $(0\bar{1}11)$. At the part of the crystal where the projected width of the twin boundary is 1000 Å, the thickness of the crystal was calculated to be 2600 or 400 Å depending upon which plane was selected. The general appearance of the micrograph and the presence of Kikuchi lines on the diffraction pattern suggest that the crystal thickness is certainly greater than 400 Å, indicating that the twin boundaries are probably $(\bar{1}101)$ planes.

Plates 2 and 3 show that in amethyst the Brazil twin individuals can be as narrow as 300 Å, but more generally they are of the order of 1000 Å.

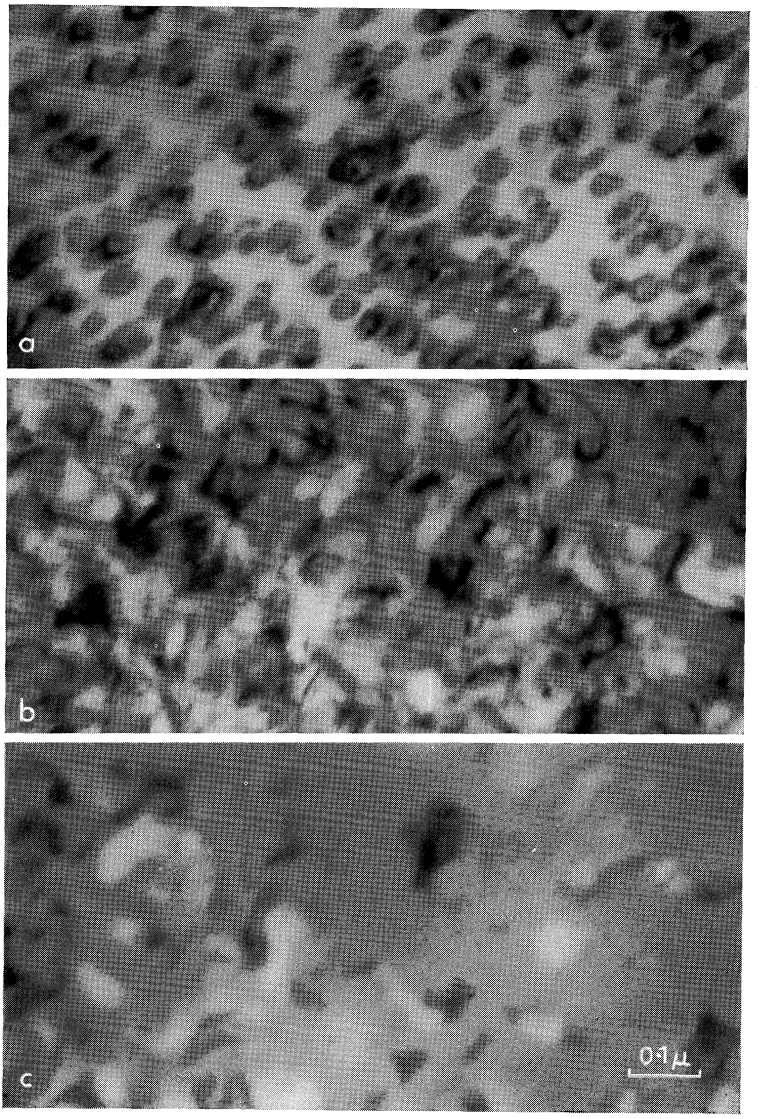
Using selected area diffraction the inclined plane defects in citrine shown in Plate 4, Figure 1, were also identified as Brazil twin boundaries, the composition plane being $(11\bar{2}0)$. Brazil twins were common in some crystals of citrine but did not occur as frequently as in amethyst.

The decoration of the Brazil twin boundaries suggests that, if our conclusions of the previous section are valid, there is a concentration of the impurity responsible for the colour along the twin boundaries. This is consistent with our earlier observation that Brazil twins are more common in the deeper coloured regions of the crystals. However, Plate 4, Figure 2, shows that in some crystals bands of impurities occur independently of the twin boundaries.

Although some crystals of amethyst show the normal uniaxial interference figures, other crystals show an anomalous biaxial character with the angle (2α) between the optic axes ranging up to 35° (Frondel 1962). Recently, Melankholin and Tsinober (1963) investigated specimens of synthetic amethyst with a polarizing microscope and established that the anomalous biaxial character was observed only near Brazil twins and, in consequence, was connected with them. The largest value of 2α observed was 7°. Melankholin and Tsinober concluded that the biaxial character was not caused by the twinning itself but was due basically to a misorientation of the left- and right-handed individuals of the twins.

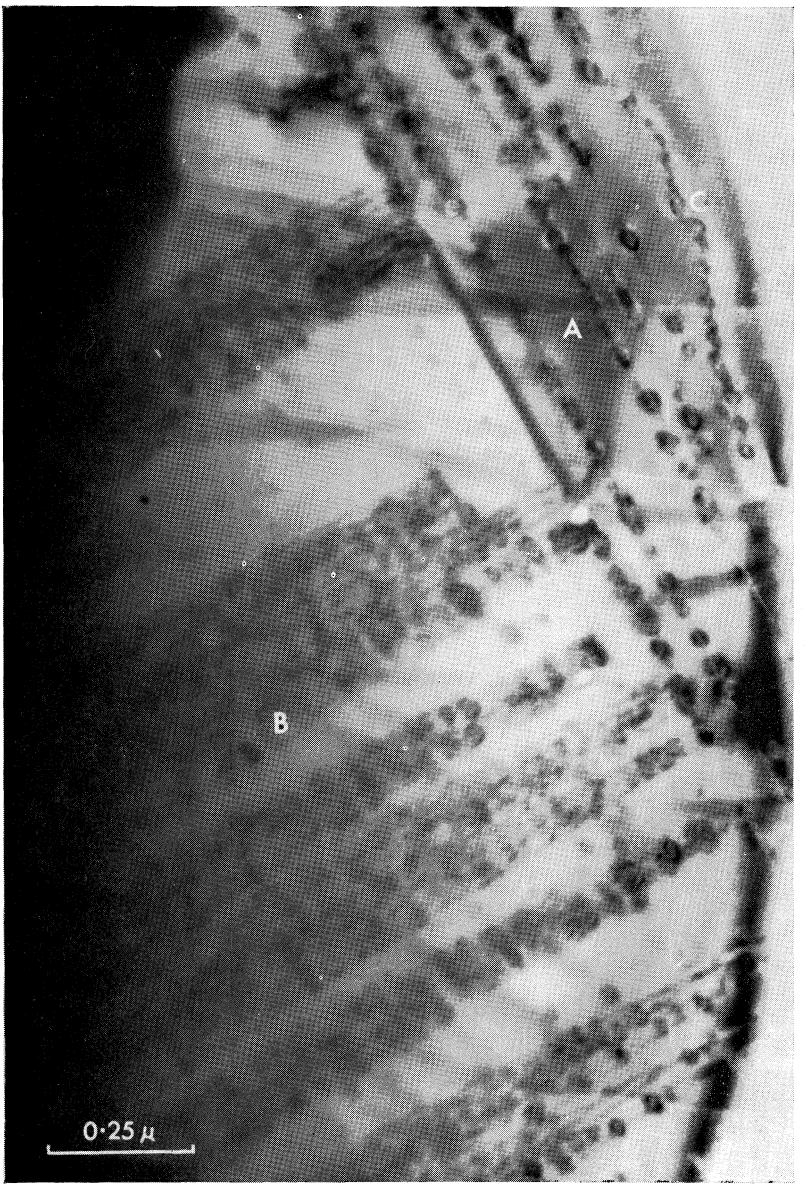
Now, since the wavelength of 100 kV electrons is 0·037 Å, the Bragg angles (2θ) in quartz will range from about 0·5° for $d = 4{\cdot}255$ Å up to 3° for $d = 0{\cdot}700$ Å. It follows that any small difference of orientation of the individuals of a Brazil twin will show up strongly as a change of contrast across the boundary. Examination of Plates 2 and 3, and Figure 1 of Plate 4, and many other electron micrographs failed to reveal any such change of contrast across the twin boundaries. Therefore, if any

ELECTRON MICROSCOPE STUDY OF AMETHYST AND CITRINE



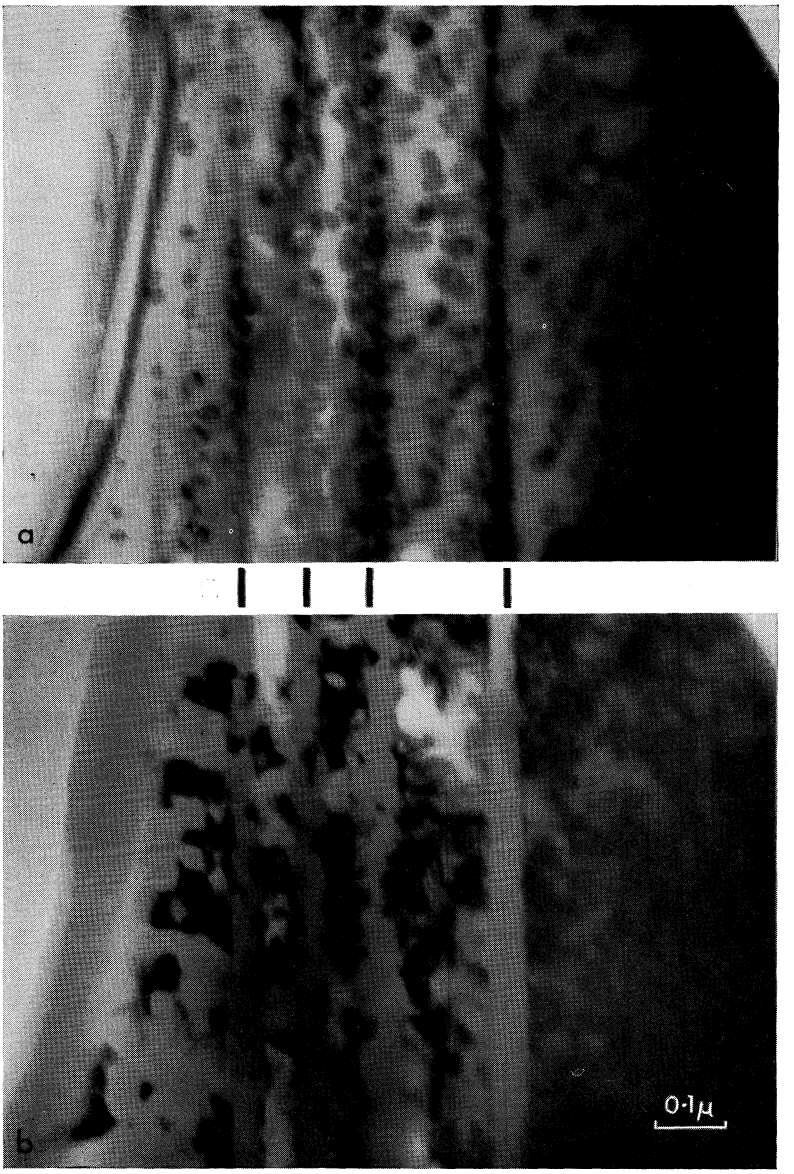
The successive stages of the damage produced in amethyst during observation in the electron microscope. (*a*) Loops formed after a few minutes; (*b*) coalescence of the loops; (*c*) disappearance of diffraction contrast due to transformation to the amorphous state.

ELECTRON MICROSCOPE STUDY OF AMETHYST AND CITRINE



Damage-decorated line defects (A) and plane defects (B) in amethyst. Both types of defect were subsequently identified as Brazil twin boundaries. The irregularly shaped decorated line at C is probably a dislocation.

ELECTRON MICROSCOPE STUDY OF AMETHYST AND CITRINE



(*a*) Damage-decorated line defects in amethyst.

(*b*) The same area as (*a*) after further irradiation. Notice that the transformation to the amorphous state has taken place preferentially along the line defects.

ELECTRON MICROSCOPE STUDY OF AMETHYST AND CITRINE

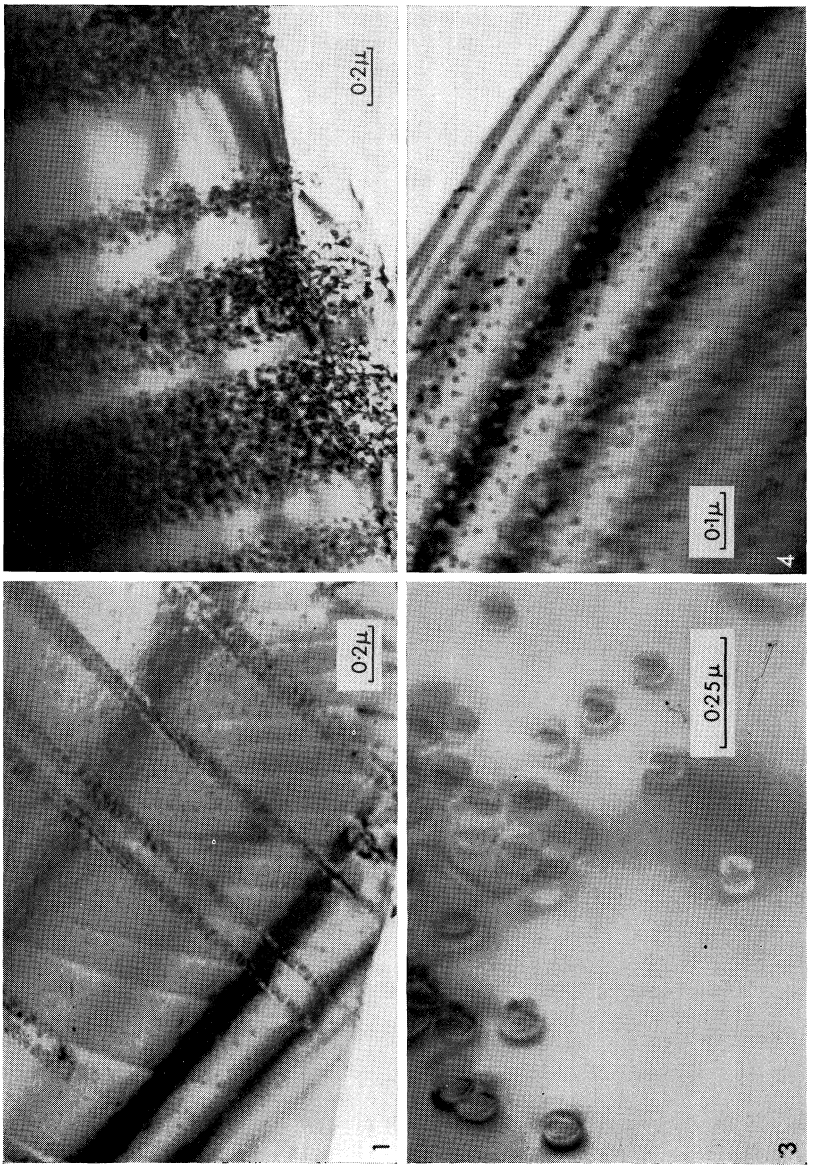


Fig. 1.—Plane defects, subsequently identified as Brazil twin boundaries, in natural citrine.
Fig. 2.—Bands of damage centres in natural citrine.
Fig. 3.—Damage centres in clear natural quartz.
Fig. 4.—Damage centres in amethyst imaged by structure factor contrast.

misorientation exists, it is much too small to account for the observed biaxial character. Our electron microscope observations show that the concentration of twin boundaries is much higher than suspected from optical observations. If there is strain associated with the twin boundaries then the overall strain in the crystal may be sufficient to produce the observed biaxial character.

V. Acknowledgments

We thank Miss J. Myers and Mr. Ted Koller for gifts of crystals, and Mr. D. R. Hutton and Mr. G. J. Troup, of this Department, for permission to quote unpublished results. We are also most grateful to Dr. R. I. Garrod, Dr. H. L. Wain, and Dr. J. V. Sanders for their critical comments.

VI. References

Ashby, M. F., and Brown, L. M. (1963*a*).—*Phil. Mag.* **8**: 1083.
Ashby, M. F., and Brown, L. M. (1963*b*).—*Phil. Mag.* **8**: 1649.
Bursill, L. A., and McLaren, A. C. (1965).—*J. Appl. Phys.* (in press).
Evans, T. (1962).—Paper No. 10, Diamond Conference, Cambridge, England.
Evans, T. (1963).—*Phil. Mag.* **8**: 1235.
Fleet, S. G., and Ribbe, P. H. (1963).—*Phil. Mag.* **8**: 1179.
Frondel, C. (1962).—"Dana's System of Mineralogy." Vol. 3. (Wiley: New York.)
Hutton, D. R. (1964).—*Phys. Letters* (in press).
Melankholin, N. M., and Tsinober, L. I. (1963).—*Kristallografiya* **8**: 110.
Thomas, G. (1962).—"Transmission Electron Microscopy of Metals." (Wiley: New York.)