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ELECTRON MICROSCOPE STUDY OF DAUPHINE MICROTWINS FORMED IN SYNTHETIC QUARTZ

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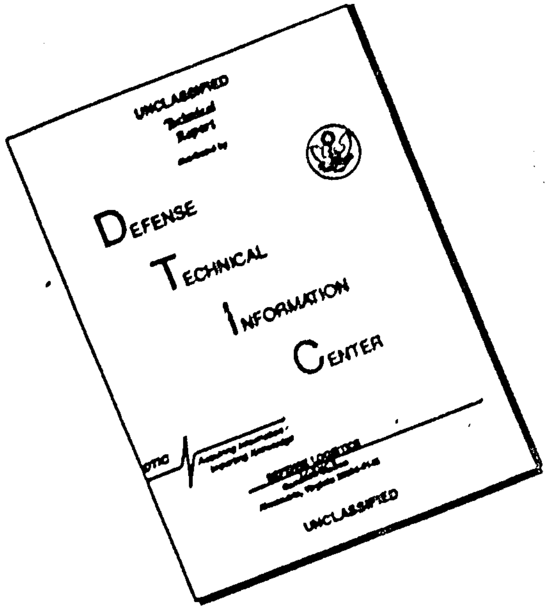

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13. ABSTRACT

Specimens of synthetic quartz were examined by transmission electron microscopy. Dauphine twins in (0001) sections, produced by cooling through the inversion temperature, were decorated at the boundaries by black spots caused by radiation damage in the microscope. These boundaries were straight lines following crystallographic directions. A misorientation between twins and matrix accounts for intensity differences between the two regions. The results are compared with those obtained with (1120) sections where fringe contrast at the twin boundary occurs because of differences in extinction distance for certain reflections. Smaller, more numerous twins were formed in electron damaged regions during examination in the microscope.

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KEYWORDS: Quartz, Microtwins, Electron microscopy, Specimen damage, Inversion twinning

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Specimens of synthetic quartz were examined by transmission electron microscopy. Dauphiné twins in (0001) sections, produced by cooling through the inversion temperature, were decorated at the boundaries by black spots caused by radiation damage in the microscope. These boundaries were straight lines following crystallographic directions. A misorientation between twins and matrix accounts for intensity differences between the two regions. The results are compared with those obtained with (11$\bar{2}$0) sections where fringe contrast at the twin boundary occurs because of differences in extinction distance for certain reflections. Smaller, more numerous twins were formed in electron damaged regions during examination in the microscope.

1. Introduction

Dauphiné twinning in quartz, also known as "electrical twinning", is very common. It occurs either during growth or can be produced artificially from β-quartz by cooling through the inversion temperature of ~573 °C. Other methods of producing Dauphiné twins include thermal shock by quenching from 200 °C or higher, and the application of pressure or thermal gradients[1]). The twinned parts are related as by a rotation of 180° around the *c*-axis and are of the same hand. The composition planes are the {10$\bar{1}$0}. Although the crystal axes remain parallel, the electrical polarity of the piezoelectric *a*-axis is reversed in the twinned parts. Because the axes do remain parallel electron diffraction patterns obtained on both sides of a twin boundary appear the same and cannot be used to identify twinning. Dauphiné twins cannot be detected by optical methods but are visible on suitably etched specimens because of a difference in texture between the twin and matrix. Macroscopic Dauphiné twins have been identified by Lang using X-ray topography[2]), and Dauphiné microtwins were found by McLaren and Phakey in natural quartz by means of transmission electron microscopy[3]). Detection by these methods was possible because the twins have different structure factors and extinction distances for certain reflections. No evidence was presented showing that Dauphiné microtwins are formed on cooling through the α–β inversion temperature.

Recently, interest has centered on the possible role of Dauphiné microtwins in the transformation of trigonal α-quartz to hexagonal β-quartz at ~573 °C[4]). Also, it has been suggested that Dauphiné microtwins form during irradiation of quartz by fast neutrons at fluences between 10^{19}–10^{20} n/cm^2 (ref. 5). Imaging and identification of these microtwins by transmission electron microscopy becomes important in assessing the results of direct heating of quartz as well as indirect thermal effects such as might be caused by exposure to radiation.

The purpose of the present paper is to show that: (1) Dauphiné microtwins, a few microns or less in size, can be formed by heating and cooling through the inversion temperature, (2) twin regions can be recognized by electron microscopy, even in the absence of fringe contrast, and (3) microtwinning is indeed enhanced in electron-damaged regions. Comparisons are made between images of (0001) and (11$\bar{2}$0) sections.

2. Experimental

The specimens examined in this study were grown hydrothermally by Western Electric and contained aluminum, sodium and lithium. Rectangular sections 10×20 mm were cut parallel to (0001) and (11$\bar{2}$0) planes and polished to a thickness of 10 mil. Discs

3 mm in diameter were cut from these sections with an ultrasonic cutting tool. Holes with thin edges were then made in the discs by mechanical polishing and chemical etching. Annealing was done in air at 680 °C. The rate of cooling to room temperature was ~7°/min. Damage to the crystal, caused by 100 kV electrons, occurred during examination. This damage, visible as black spots, was first reported by McLaren and Phakey[6]).

The image obtained by structure factor contrast showed that the spots are associated with a decrease in the effective thickness of the crystal. The authors interpreted this as indicating the presence of centers of amorphous silica. Furthermore, they believed that these spots formed preferentially where the concentration of Fe^{3+} ions was highest in amethyst and citrine quartz as, for example, along twin boundaries. In the present study of synthetic quartz, black spots appeared after about one minute at a flux of 10^{17} e/cm^2/sec. This flux was achieved with the beam focussed to a 2 μm diam. spot on the specimen. With increasing fluence, the electron diffraction pattern shows a broadening of the Kikuchi lines and finally their disappearance. At a fluence of 10^{20} e/cm^2 large patches of amorphous regions are observed and the diffraction pattern contains both diffuse rings and spots from the regions which are still crystalline. Because of the relatively low energy of the electron beam it is believed that the damage is due primarily to thermal effects.

3. Results and discussion

In the work of McLaren and Phakey, Dauphiné twins in natural quartz were identified by fringe patterns bonding the twin, visible when quartz fragments could be oriented to give strong $\{10\bar{1}1\}$ or $\{10\bar{1}2\}$ reflections. An explanation was given in terms of differences in extinction distance between twin and matrix for these reflections.

3.1. (0001) Sections

In preliminary results described elsewhere[7]) it was shown that when (0001) sections of quartz cooled through the inversion temperature were examined in the electron microscope black damage spots formed preferentially in straight lines. The lines followed crystallographic directions enclosing domains which differed in intensity from the matrix upon tilting. A typical example is seen in fig. 1. Using selected area diffraction, patterns were obtained from regions A and B and the shift of the Kikuchi lines indicated a misorientation of ~22 min of arc. Further results to be described in this paper support the contention that these domains are Dauphiné microtwins.

Although the decorated regions often extended to the hole through the specimen many examples of twins surrounded by the matrix were observed. One of these is shown in fig. 2 where the twin region is defined both by damage spots and intensity differences. In many examples strong contrast was obtained for $\{30\bar{3}0\}$ type reflections as shown in fig. 3. Lang has demonstrated how $(30\bar{3}1)$ and $(30\bar{3}\bar{1})$ reflections in X-ray topography of quartz reveal Dauphiné twins because of differences in structure factor which cause significant differences in intensities[2]). But for $\{30\bar{3}0\}$ reflections the structure factor is the same for twin and matrix, therefore no intensity differences should be noted when imaging with these reflections. It appears that the observed

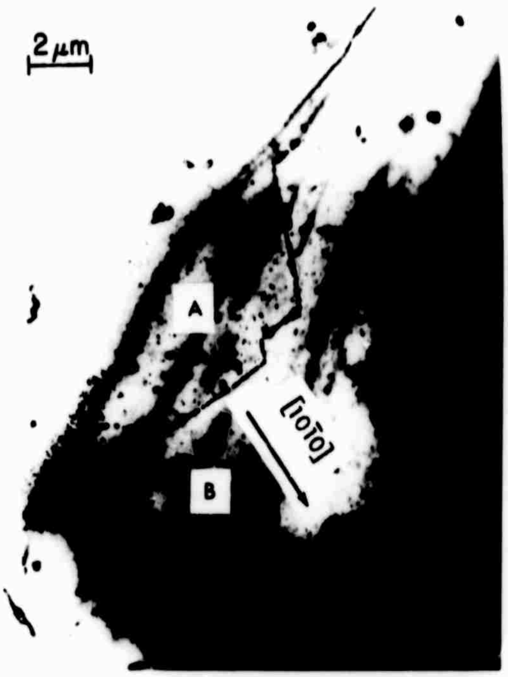

Fig. 1. (0001) Quartz. Boundary decorated by radiation damage spots. Diffraction patterns from regions A and B indicate a misorientation.

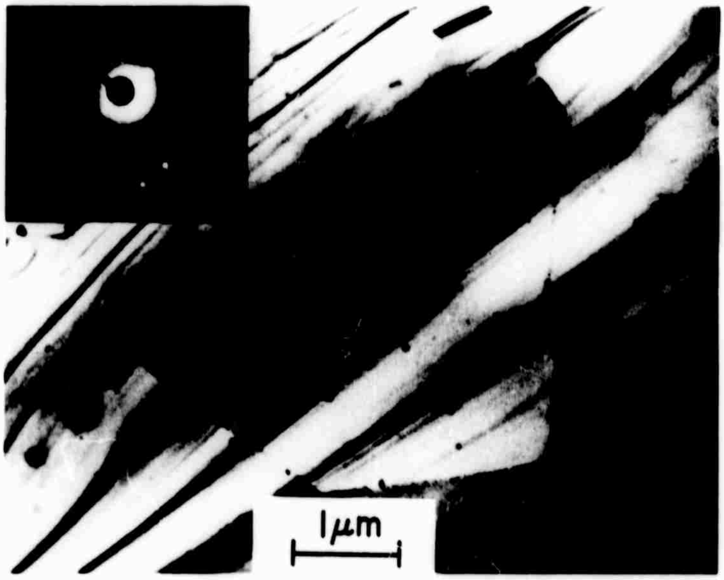

Fig. 2. (0001) Quartz. Twin surrounded by matrix visible by difference in intensity as well as by boundary decoration. Formed by cooling through the inversion temperature.

contrast arises from the aforementioned misorientation between twin and matrix.

Dauphiné twins can be removed by heating above the inversion temperature while new ones may be formed on cooling below that temperature. The results of a second annealing of a specimen containing decorated boundaries provided evidence that they encompassed Dauphiné twin regions. Fig. 4a is a micrograph showing a decorated boundary. Differences in intensity across the boundary are clearly seen. Fig. 4b shows the same region after annealing to 680 C for 2 hr and cooling to room temperature. Where originally the twin boundary had existed there is only a path of damage centers, not affected by the anneal. New twins are clearly seen by intensity differences.

3.2. (11$\bar{2}$0) Sections

Other evidence of Dauphiné microtwin formation was provided by annealing (11$\bar{2}$0) sections of quartz. In this orientation it was possible to satisfy the conditions for fringe visibility by obtaining {10$\bar{1}$1} and {10$\bar{1}$2} type reflections. Fig. 5a and 5b show Dauphiné twins in an as-received specimen and in an annealed specimen respectively.

3.3. Effect of electron beam on twinning

Having established that the straight lines of damage centers in (0001) sections enclose Dauphiné twins it is shown that these twins occur with a greater density in regions heavily damaged by the electron beam. The twin boundaries were usually visible after removing the specimen, annealing in air and cooling through the inversion temperature. An example of this is seen in fig. 6, showing a specimen which had been subjected to 100 kV electrons to a fluence of 5×10^{20} e/cm^2. Normally, the damage centers increase in size with increasing exposure but not in number. However, after annealing and further exposure to the beam, new spots, identifiable by their smaller size, form along the twin boundaries. The annealing, in effect, conditions the specimen so that new damage centers can form, but only along the twin boundaries. The present results give no indication that damage is related to location of impurity ions as proposed by McLaren and Phakey. However, if there is a correlation between damage and impurity location it is necessary to accept the idea that diffusion of impurities to the twin boundaries occurs during annealing or heating in the electron beam. This

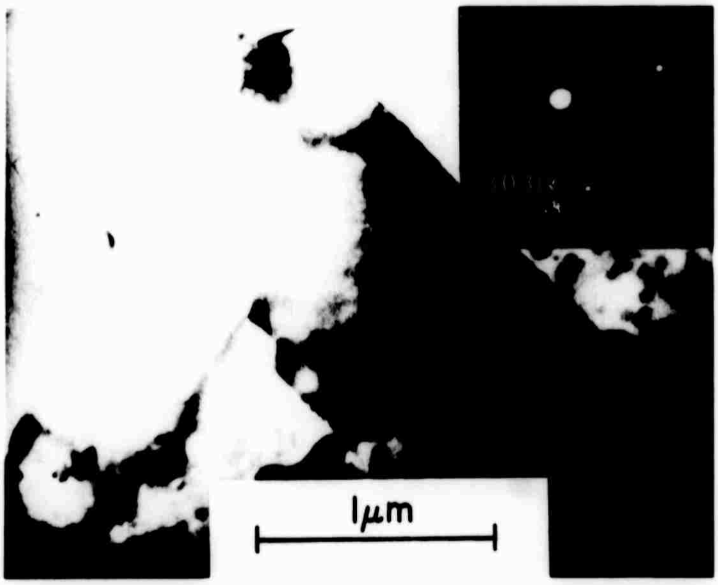

Fig. 3a. (0001) Quartz. Dauphiné twin formed during examination in the electron microscope.

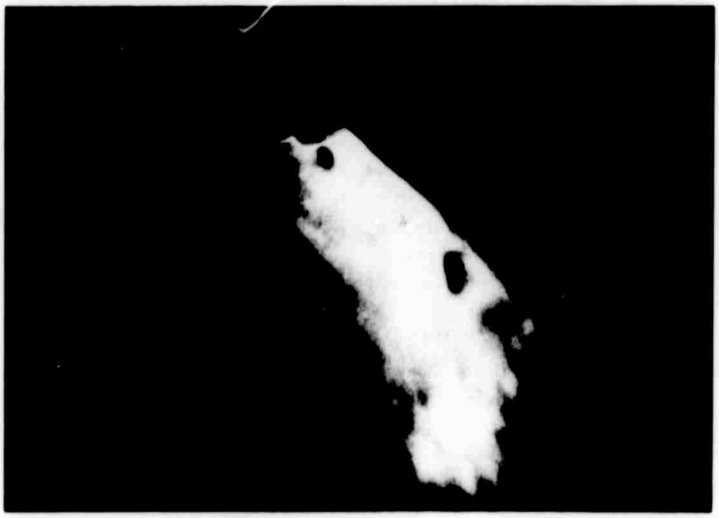

Fig. 3b. Dark field image using the (30$\bar{3}$0) reflection.

might be possible with Li^+ or Na^+ but is unlikely with Al^{3+} (ref. 8).

Some Dauphiné twins were formed during examination in the electron microscope without subsequent annealing. Here also the greatest density of twins occurred in the region of radiation damage. Fig. 7 shows twin boundaries which appeared in a (0001) section. Note that the spots outlining the boundaries are again much smaller than the randomly arranged ones, indicating that twinning and decoration occurred some-

Fig. 4a. (0001) Quartz. Dauphiné twin formed by cooling through the inversion temperature.

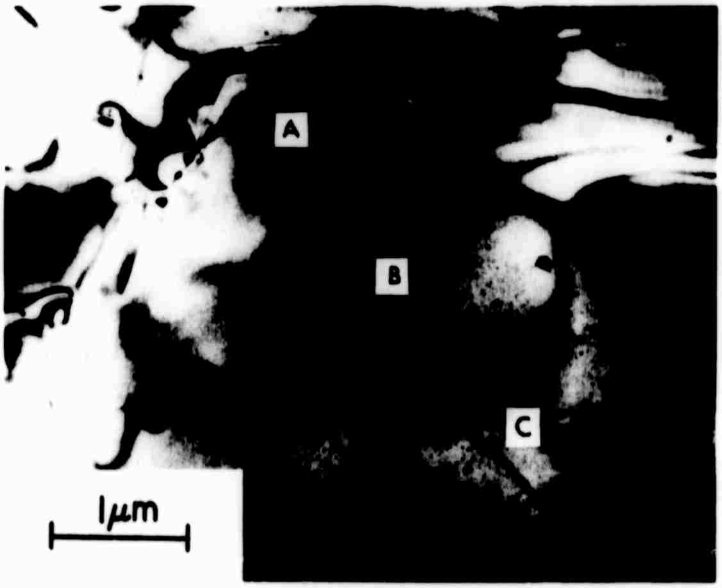

Fig. 4b. Same region shown in (a) after second annealing. The original twin has been removed and only the black damage spots which had formed at the boundary remain at A B C. New twins visible by difference in intensity cross the boundary of the original twin.

Fig. 5a. (11$\bar{2}$0) Quartz. Dauphiné twin in as-received specimen showing electron damage spots. The fringes distinguishing the twin boundaries were detected before damage spots appeared.

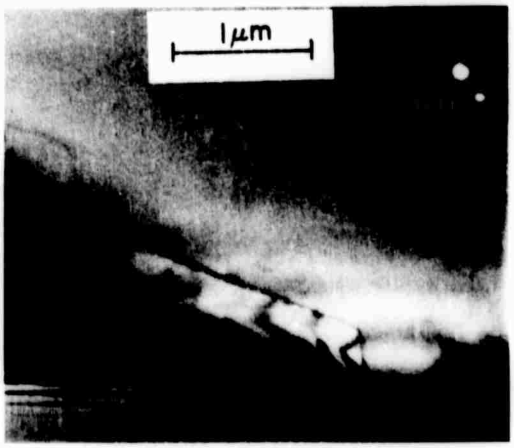

Fig. 5b. (11$\bar{2}$0) Quartz. Dauphiné twin formed by cooling through the inversion temperature. Fringe contrast is visible with a strong (10$\bar{1}$1) reflection.

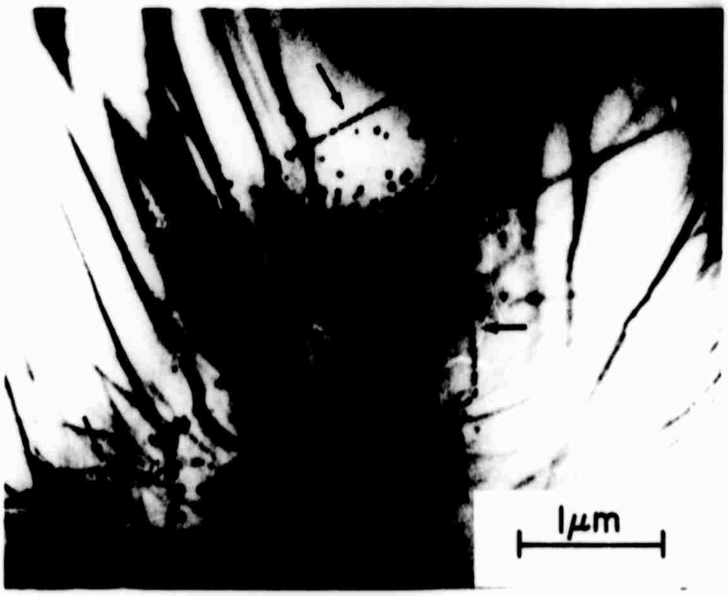

Fig. 6. (0001) Quartz. Specimen highly damaged by fluence of 10^{20} e/cm^2. Subsequent cooling through the inversion temperature developed new damage spots revealing twin boundaries shown by arrows.

time after the initial damage by the electron beam. The possibility exists that local temperatures in the specimen during examination could exceed the inversion temperature and the actual twinning would result on cooling. On the other hand, twinning could have occurred in the region as a result of the damage. Subse-

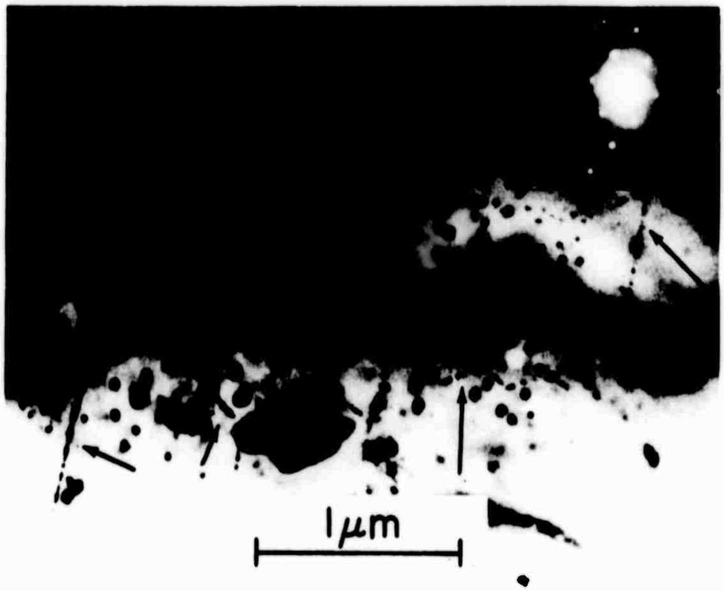

Fig. 7. (0001) Quartz. Highly-damaged region of specimen. During the examination new spots developed along crystallographic boundaries (arrows) revealing Dauphiné twins.

quent heating in the beam could cause diffusion of impurities to the twin boundaries where new damage centers form to decorate them.

Similar extensive twinning was observed in $(11\bar{2}0)$ specimens after several minutes exposure to the electron beam without subsequent annealing. Twin boundaries were usually detected by fringes obtained with $(10\bar{1}1)$ reflections, but sometimes differences in contrast were also found for twin and matrix. In fig. 8a fringes bounding the twin region are clearly observed with a strong $(10\bar{1}1)$ reflection. By tilting away from this condition, fig. 8b, the fringes are out of contrast but there is contrast between twin and matrix. The contrast would be more uniform in the absence of the damage centers.

In trying to explain the preferential twinning in the electron damaged region one must consider what type of disorder can occur as the result of high fluences of 100 kV electrons on quartz, particularly if the damage caused to the crystal is due mainly to thermal energy within the small regions of the crystal under examination. In studying the mechanism of the phase transition, α to β, in quartz Young found that the specimen behaved as though it contained numerous microtwins of the Dauphiné type just below the inversion temperature from which condition it could readily transform to the hexagonal β-phase[4]). Comes et al suggested that a rearrangement of the SiO_4 tetrahedron in fast neutron irradiated quartz to form Dauphiné microtwins would explain the disorder they observed by X-ray diffraction[5]). Above 10^{19} n/cm^2 the disordered phase consisted of highly perturbed matter embedded in a crystalline matrix. The crystal at this stage has a hexagonal symmetry. Above 10^{20} n/cm^2 the crystalline pattern disappears and the diffuse ring indicates vitreous silica. The results appear to parallel those obtained with 100 kV electrons. If the energy of the electron beam is sufficient to thermally excite the specimen to bring about displacements of the SiO_4 tetrahedron as evidenced by the presence of amorphous regions then it is possible that the necessary conditions for rotation of the SiO_4 tetrahedron to bring about the α_1 to α_2, or twin condition, will be achieved in some parts of the specimen.

4. Summary and conclusions

Dauphiné microtwins identified by transmission electron microscopy were formed in synthetic quartz

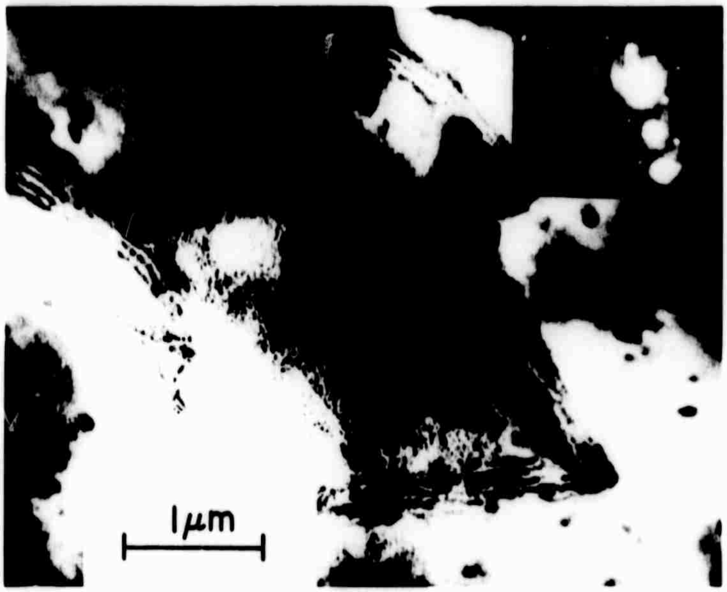

Fig. 8a. $(11\bar{2}0)$ Quartz. Twinning which occurred during examination of the specimen. Strong $(10\bar{1}1)$ reflection shows fringe contrast.

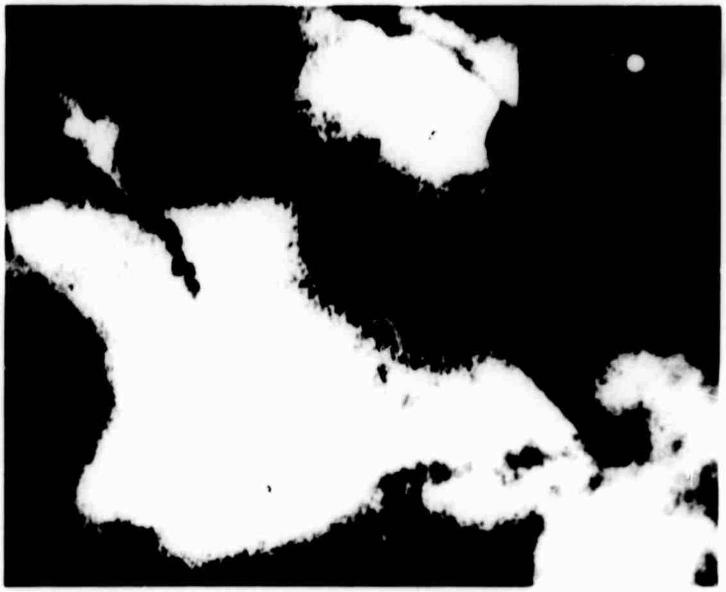

Fig. 8b. Tilting the specimen causes extinction of the fringe contrast, but the boundary is visible because of differences in intensity between twin and matrix.

which had been cooled through the inversion temperature. These twins are not readily detected by light microscopy of etched specimens or X-ray topography because of their small size. Those observed in (0001) sections exhibited straight line boundaries parallel to crystallographic directions which became preferred sites for radiation damage caused by the electron beam. If the damage at these sites is related to concentrations of impurity ions, as suggested by McLaren and Phakey, it appears that diffusion occurs during examination of the specimen.

By slight tilting of the specimen so that the beam was no longer strictly parallel to the c-axis it was possible to show differences in intensity between twin and matrix. It was established that under these conditions, where for example the operating reflection was $(30\bar{3}0)$, the difference in intensity reflects the misorientation between twin and matrix.

It was found by examining both (0001) and $(11\bar{2}0)$ sections that smaller, more numerous microtwins form in parts of the crystal highly damaged by the electron beam. It is suggested that the disorder caused by the radiation might leave parts of the specimen in the condition where SiO_4 tetrahedra could rotate to the position occupied in Dauphiné twins. This is essentially the idea proposed by Comes et al. to explain the results of fast neutron bombardment of quartz.

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