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The tensile fracture of quartz crystals

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Quartz crystals of five orientations have been fractured in tension at temperatures below 800 K in air and water-free environments. The radius of the initial crack nucleus determines the fracture stress which, in turn, controls the velocity–distance relationship. The unusual fractography is described in which fracture occurs predominantly along facets of the rhombohedral planes and requires a surface energy of 2 J m^{-2}.

1. Introduction

The purity, perfection and the resistance to plastic flow at low temperatures make synthetic α-quartz crystals ideal for the investigation of brittle fracture. The chemical similarities with glass allow a close comparison between fracture behaviour of crystalline and amorphous solids. An examination of the fracture behaviour of quartz is valuable from the technological point of view since quartz provides an important electrical device material and the mining of minerals often involves the blasting, cutting and comminution of quartzite. Studies of the plastic deformation by the uniaxial compression of single crystals of quartz have confirmed that dislocation generation and movement are only possible under atmospheric pressure at temperatures above 820 K [1]. However, plastic flow has been induced at lower temperatures (~600 K) if a superimposed hydrostatic pressure prevents fracture [2]. A number of workers have examined the fracture of single crystals during compression and indentation [3–5] and a statistical investigation of cleavage was made by Bloss and Gibbs [6]. These have led to the conclusion that quartz possesses no distinct cleavage plane although a preference was shown for fracture along the positive and negative rhombohedron planes, $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$ repectively. The present paper describes the fracture behaviour of quartz crystals tested in tension and the known influence of water on the fracture of silica glass [7, 8] suggested that the investigation of quartz should be made as a function of environment.

2. Experimental

Single crystals of synthetic and natural quartz were sliced with a diamond saw into specimens with five distinct crystallographic orientations (Fig. 1) and with dimensions 60 mm × 10 mm × 1 mm. After polishing the surfaces with 1 μm alumina, approximately 1 mm deep notches were cut in the narrow faces at the mid-point of the specimens with a 0.05 mm thick annular diamond saw. The cutting pressure was very small and care was taken to avoid vibrational and distortional stresses. The diamond grit of the cutting wheel was quoted by the manufacturers to be less than 60 μm. The end of the notch was square but scanning electron microscopy revealed the presence of

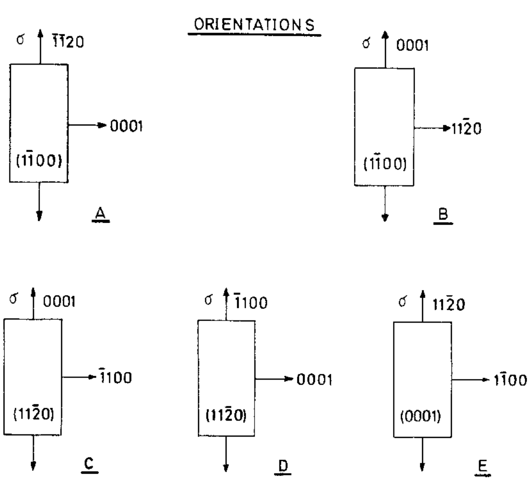


Figure 1 The five orientations (A, B, C, D, E) of the crystals which were fractured by a tensile stress applied in the direction of the long edges.

fine cutting grooves. Sharp notches of starting cracks were produced in a number of specimens by thermal shock treatments.

The specimens were mounted on freely rotating gimbal attachments of the tensile machine using "Eastman's 910" adhesive for tests at ambient temperatures and below, and "Aremco Ceramacoat 512" ceramic adhesive for the elevated temperature tests. The experiments were carried out under liquid nitrogen at 77 K, water-free toluene for temperatures up to room temperature, and in a vacuum of better than 10^{-4} mm Hg for room temperature and above. The temperature of the toluene was attained by passing liquid nitrogen around the copper container and the elevated temperatures *in vacuo* were obtained by a resistance wire furnace. A number of room temperature tests were performed in air. In order to test the influence of water at the notch tip prior to testing, several specimens were out-gassed in a vacuum of better than 10^{-5} mm Hg at 473 K for 24 h and then mounted, without exposing the notch to the atmosphere, and tested under toluene. All tests were carried out in uniaxial tension at a strain-rate of approximately 7×10^{-5} sec^{-1}. The load at fracture was recorded and the original notch lengths to the point of bifurication were measured by photographing at a magnification of × 100. The fracture surfaces were examined by both optical and scanning electron microscopy. Fine features such as Wallner lines were photographed by optical differential interference techniques.

The velocity of crack propagation was determined by the resistance grid method and by an analysis of Wallner lines which included the effects of crystal anisotropy [9] (see Field [10] for a discussion of these methods). A grid of 36 lines of "Nichrome" was vapour deposited perpendicular to the expected fracture path. The line at the tip of the notch acted as a trigger for the recording oscilloscope and the remaining lines were connected to a circuit which differentiated the sudden change in voltage as each line of the grid was broken during crack propagation. The piezoelectric quartz crystals develop electric charges on their surfaces on account of strain changes which occur during fracture. In order to avoid the interference of this effect with the resistance grid signals, crystals of orientation E (Z cut) were chosen for these velocity experiments. The crystal symmetry of this orientation is such that piezoelectric charges are not developed on the specimen faces on which the resistance grids were deposited.

3. Results and discussion

3.1. Fracture strength

The results of the tensile tests performed *in vacuo* or toluence are presented in Fig. 2; the product of the stress at fracture σ_f and the square root of the initial notch or crack length (c_0) is plotted as a function of temperature. Included in the same figure are values of the product of the fracture stress and square root of the crack length at the point of branching (c_b) for those specimens in which the crack bifurcated. The majority of the values fall between the curves which have been drawn and it can be seen that the temperature dependencies of $\sigma_f c_0^{\frac{1}{2}}$ and of $\sigma_f c_b^{\frac{1}{2}}$ show plateaux

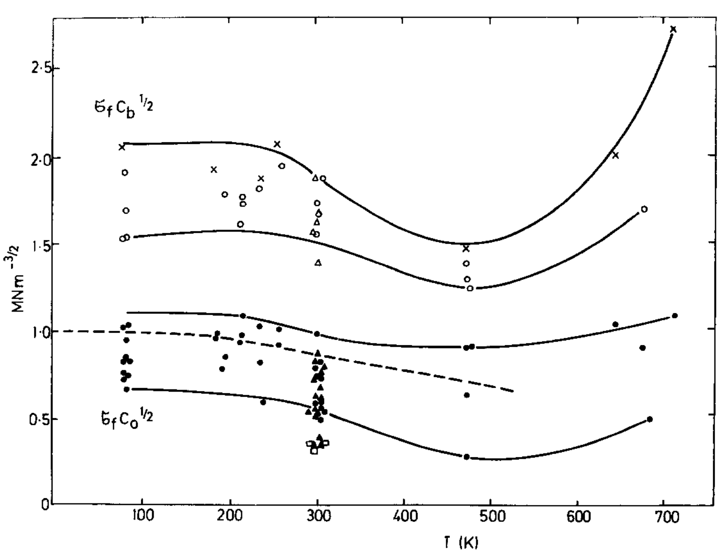


Figure 2 The temperature dependence of the fracture stess σ_f expressed as the products $\sigma_f c_0^{1/2}$ (closed circles) and $\sigma_f c_b^{1/2}$ (open circles) where c_0 is the initial notch length and c_b is the crack length at the point of crack bifurcation. The points (marked X) are values of $\sigma_f c_b^{1/2}$ for specimens of orientation C (see Fig. 1). The results for the "sharp" cracks are shown by squares (□) and the results for experiments performed in air are shown by triangles (△, ▲). The broken line represents the value of σ_f/σ_f^0 given by the theoretical model of Gilman [17] (see text).

at low temperatures and minima around 500° K. The ratio $\sigma_f c_b^{\frac{1}{2}}/\sigma_f c_0^{\frac{1}{2}}$ has a value of about 2. The average of $\sigma_f c_0^{\frac{1}{2}}$ for specimens tested in air at room temperature was found to be 0.60 MN $m^{-3/2}$ and is somewhat lower than that for specimens tested in toluene or *in vacuo.* The value of 0.35 MN $m^{-3/2}$ was found for the specimens containing sharp thermally induced cracks and tested in toluene at room temperature. There was no systematic influence of de-gassing the quartz specimens before testing and no significant difference in value obtained for synthetic and natural quartz crystals.

In view of the dependence of the fracture stress on the length and sharpness of the initial notch, the following treatment for the estimation of the surface energy for fracture is appropriate. For fracture to occur, the Griffith energy criterion $\sigma_f \geqslant (2E\gamma/\pi c_0)^{\frac{1}{2}}$ must be satisfied and, in addition, the concentrated stress at the tip of the crack $[2\sigma_f(c_0/r)^{\frac{1}{2}}$ where r is the radius of the initial crack tip] must exceed the theoretical bond strength given approximately by $(E\gamma/a)^{\frac{1}{2}}$, where E is Young's modulus, γ is the surface energy and **a** is the equilibrium separation of atoms. The observed fracture stress should, therefore, be given by

$$\sigma_f \simeq (E\gamma r/4ac_0)^{\frac{1}{2}}. \qquad (1)$$

Thus a crack with a tip radius of about 2.5**a** corresponds to spontaneous crack growth according to the Griffith equation. Cracks which are initially blunt will require an overstress for the process of sharpening to a Griffith crack. This overstress will result in an excess of strain energy in the specimen and a large dissipation as kinetic energy when fracture occurs.

The sharp cracks introduced by thermal shock in the quartz crystals will have tip radii approaching atomic dimensions and the measured value of ≃0.35 MN $m^{-3/2}$ for $\sigma_f c_0^{\frac{1}{2}}$ for these specimens gives a surface energy of approximately 2 J m^{-2} when the mean value of 100 GN m^{-2} for E is used in the Griffith equation. This value of surface energy agrees quite well with values calculated from bond energy data. The energy of the Si–O bond has an experimentally determined value of 36.8×10^4 J mol^{-1} [11]; thus the bond energy four-fold co-ordination is 6.2×10^{-19} J. The number of bonds per square metre lies in the range 6 to 8×10^{18} for the low index planes of quartz and hence surface energy values between 1.8 and 2.4 J m^{-2} are expected. Using a mean value of 2 J m^{-2} for γ and the experimental values of $\sigma_f c_0^{\frac{1}{2}}$ for the notched specimens, Equation 1 indicates that the crack nuclei on the notches have radii between 5**a** and 20**a**. The finer edges of the diamonds on the cutting wheel can reasonably be expected to produce grooves with radii of this size. Since the details of the crack tip geometry determine the fracture stress, the random variation of the parameter r from specimen to specimen is expected to mask any systematic variation in elastic modulus and surface energy due to crystal orientation or the difference between synthetic and natural crystals. The range of values of $\sigma_f c_0^{\frac{1}{2}}$ shown in Fig. 1 for any given temperature is, therefore, due to the range of r for the specimen.

The tendency for the notched specimens which are tested in the presence of water vapour, to fracture at lower stress values suggests that water vapour assists the sharpening of the initial cracks in the presence of an applied stress. The presence of water vapour in the notch before testing does not sharpen the cracks since a prior de-gassing treatment does not lead to a significant difference in fracture stress on subsequent testing in toluene or *in vacuo.* It is also improbable that the presence of water vapour during the test lowers the fracture stress through a lowering of the surface energy since the gaseous diffusion rate is less than the crack velocity [8].

The temperature dependence of $\sigma_f c_0^{\frac{1}{2}}$ and $\sigma_f c_b^{\frac{1}{2}}$ (Fig. 2) cannot be ascribed in full to the temperature dependence of interatomic forces which would be reflected by the values of the elastic constants and surface energy. The maximum decrease in the measured values of Young's modulus between 100 and 500 K is only 6% [12], whereas the value of $\sigma_f^2 c_0$ decreases by approximately 30%. Moreover, the modulus decrease is continuous while the fracture stress becomes independent of temperature below about 200 K. Above 500 K the elastic modulus continues to decrease in contrast to the observed increase in fracture stress. Fracture stress values have been measured as a function of temperature for other brittle materials by previous authors and minima have also been observed. (See [13] for a discussion.) The reduction of temperature sensitivity at low temperatures has also been noted [14, 15]. Since the stress for fracture is determined by the geometry or sharpness of the initial notch, the source of the observed temperature dependence must be sought in a mechanism of crack sharpening or, in the case of fracture at temperatures above the minimum, in the mechanism of crack blunting. Congleton *et al.* [16] explained the temperature dependence of the stress required for the fracture of alumina in terms of localized plastic flow at the crack tip. They argued that at lower temperatures dislocation slip or twinning might somehow be necessary for fracture propagation and thus the thermal activation of these processes would account for the experimental fracture behaviour. Our electron microscopy and X-ray topography studies have provided no evidence for such a mechanism in quartz, although it is recognized that the localized nature of the plastic flow would make confirmation difficult. However, any conventional thermal activation theories would predict a linear increase in fracture stress with decreasing temperatures and not the observed diminshing temperature sensitivity with decreasing temperature. Gilman [17] has suggested that low temperature brittle fracture can proceed by stress activated "tunnelling of the atomic bonds" at the crack tip. The increase in temperature reduces the average height of the energy barrier and an equation

$$\sigma_f/\sigma_f{}^0 = [1 - B \coth(\theta/2T)]\,(1 - B)^{-1}$$

is derived which describes the dependence of temperature (T) of the fracture stress σ_f in relation to the fracture stress σ_f^0, at 0 K. The characteristic Debye temperature θ is related to the magnitude of the energy barrier in the presence of a stress U_m by the expression $B = k\theta/2U_m$ where k is Boltzmann's constant. This equation successfully accounts for the form of the temperature dependence at low temperature of the fracture stress of Al_2O_3 filaments. The dashed line of Fig. 2 shows that observations on quartz fit such an expression when a reasonable value of $U_m = 0.1$ eV ($\sim 1.6 \times 10^{-20}$ J) is taken and $\theta = 470$ K. A stress-activated crack sharpening mechanism based on this theory may, therefore, be applicable and the stress required to sharpen a crack of a given radius to the Griffith radius will be temperature dependent in the manner observed. The presence of water at the crack tip must reduce the magnitude of the energy barrier U_m in the presence of a stress. The stress induced hydrolysis of the Si–O bonds at the tip of the crack is probably responsible for the reduced barrier.

The increase in fracture stress above 500 K is likely to be due to an increasing amount of plastic blunting by the action of the high stress concentration at the initial notch, since general macroscopic plastic deformation has been observed in uniaxial compression [1. 2] at 600 K and evidence for dislocation generation and movement was given in both publications.

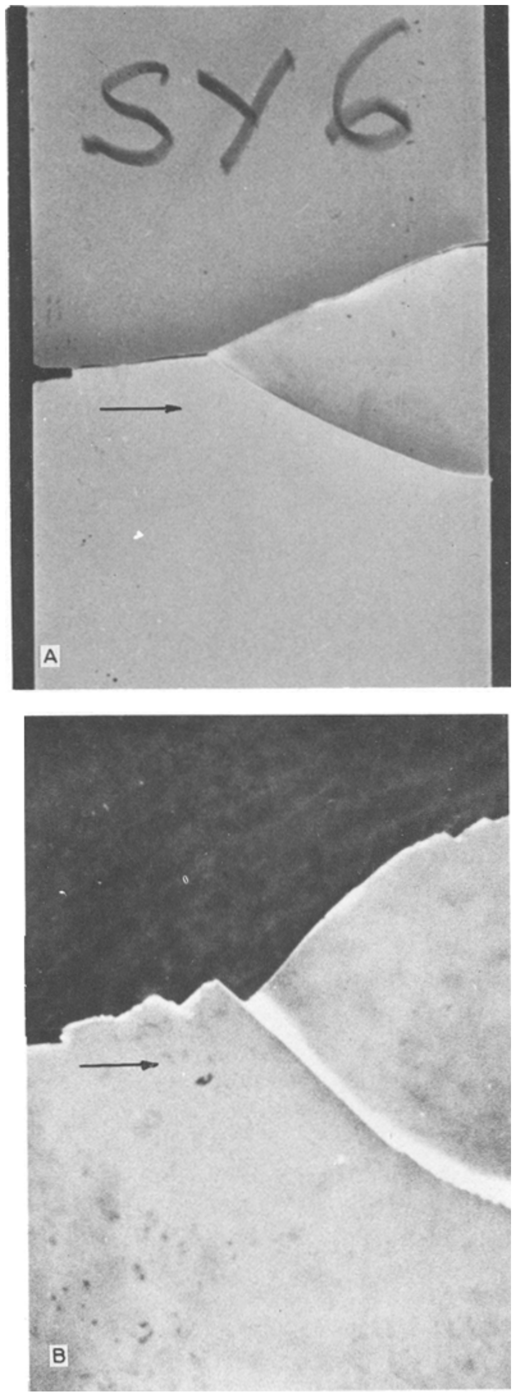


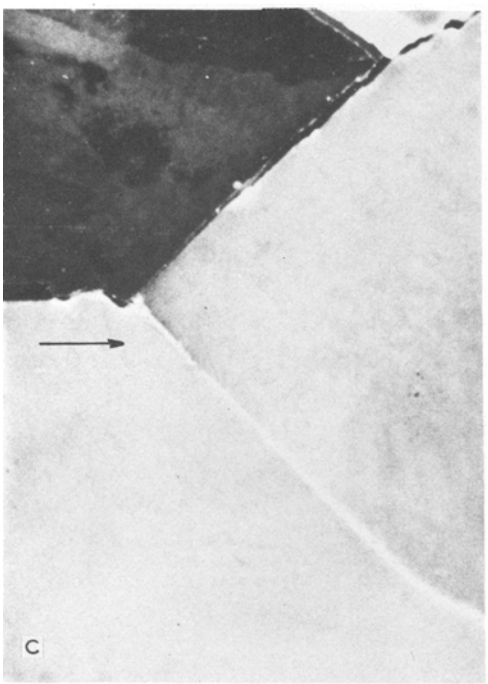
Figure 3 Typical fracture paths across the 10 mm wide faces of the specimens of the five orientations (A, B, C, D, E).

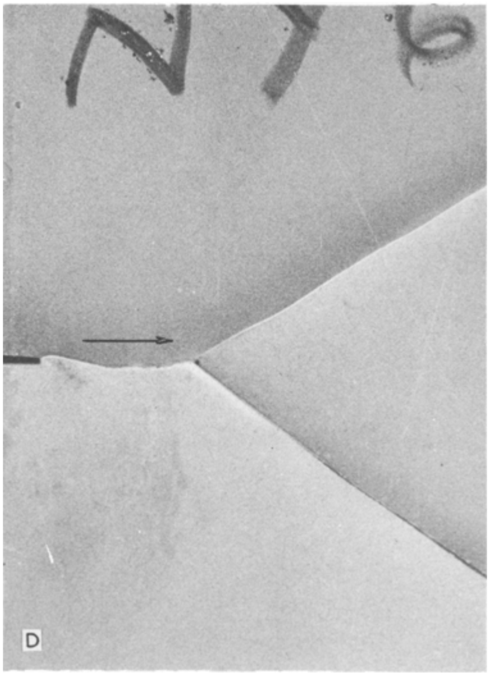
3.2. Fractography

The existence of a low energy cleavage plane in α-quartz was indicated by the behaviour of crystal wafers when subjected to thermal shock treatments. Fracture occurs by planar cleavage along a rhombohedral plane across the width of the plates. However, when tested in tension the fracture surfaces are not always planar and their exact form is determined by the direction along which the tensile force is applied, the anisotropy of surface energies for crystal planes and the magnitude and shape of the dynamic stress field at the tip of the moving crack. The detailed consideration of these influences will be subject of a future communication. Here we merely present the experimental findings.

Fracture paths, typical for each of the five crystal orientations of Fig. 1, are shown in the photographs of Fig. 3. Fracture surfaces are presented in Fig. 4. The specimens of orientations A to D are similar in that their fractures show initial flat mirror-like regions, which acquire steps or zig-zags of increasing size. If the fracture stress is sufficiently high, then the cracks subsequently bifurcate. Thus, the specimens which fractured in air or from sharp cracks at low stress values have less tendency to zig-zag or bifurcate. The cracks which propagate in a zig-zag fashion do so on two planes equally inclined to the stress axis and the size of the steps increases systematically until the fracture is completed or bifurcation occurs. If bifurcation eventuates, the branch cracks propagate on the same planes on which the zig-zag propagation occurred; this has enabled a crystallographic identification of these planes to be made.

Analysis of these planes on many specimens of





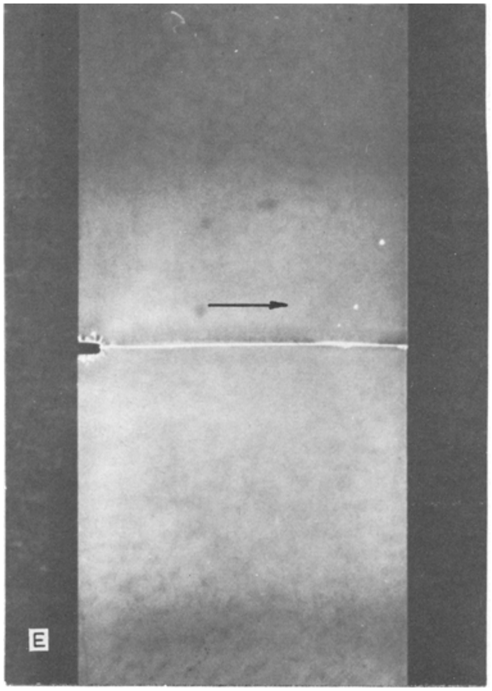
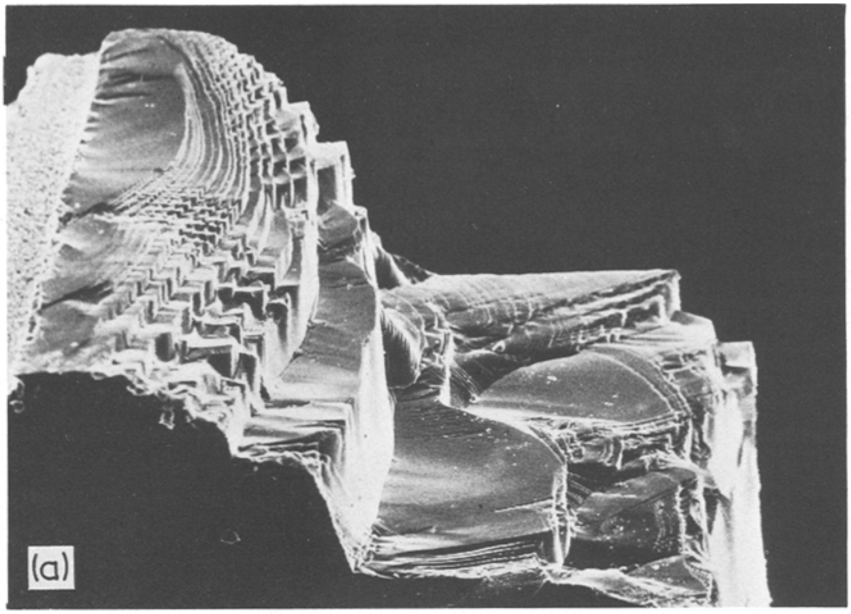


Figure 3 continued.



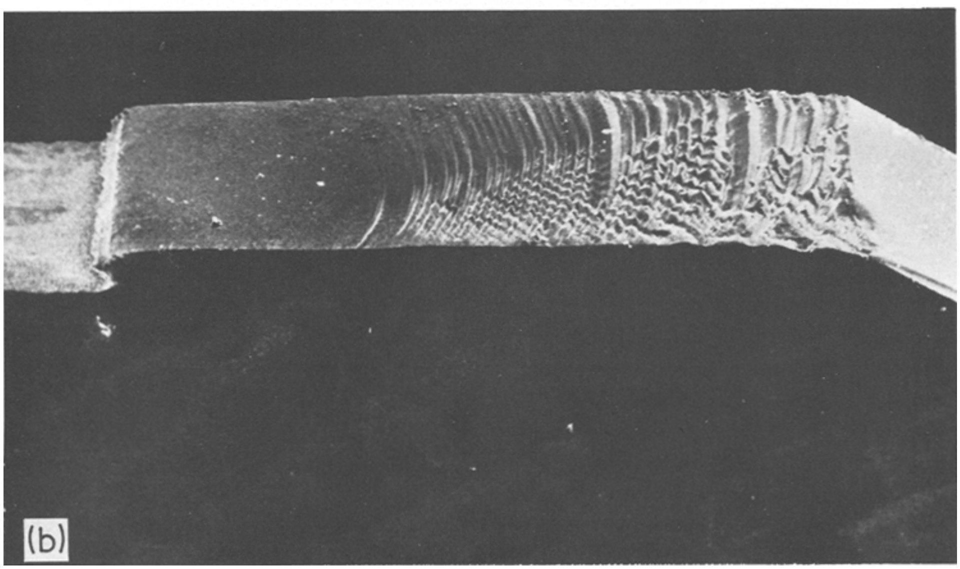
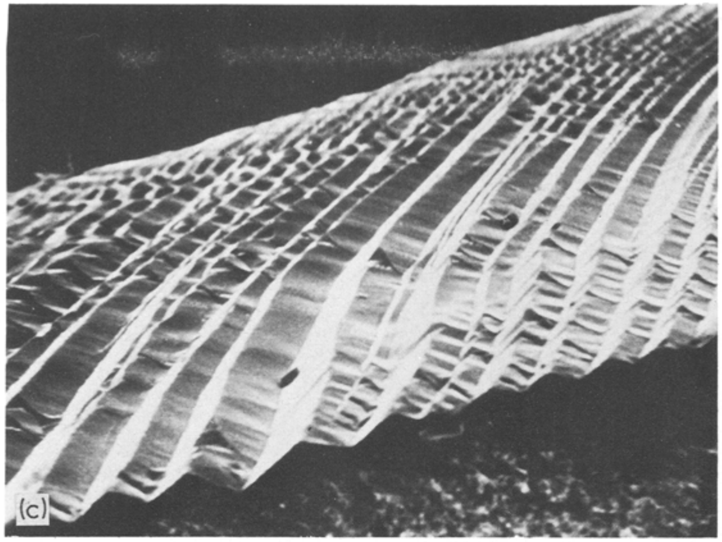


Figure 4 Fracture surfaces typical of specimens of orientations (a) B (× 100),(b) C (× 20), (c) C (× 135), (d) E (× 56). The surface of crystal E shows Wallner lines together with the values obtained for crack velocity expressed as fractions of the shear velocity (~3.8 km sec^{-1}).

each orientation A to D has been made with the aid of stereographic projections. Within the experimental error of the Laué determinations of the crystal orientations, the zig-zag and bifurcation planes can be rationalised in terms of cleavage on the rhombohedral planes. The results thus confirm previous indications [6] that quartz does possess a preferred cleavage plane, although it is very apparent from our experiments that the detailed stress field at the crack tip has an important influence.

Crystals of orientations E never fractured in a zig-zag manner and well defined bifurcation was not observed. Failure occurred in a planar fashion along the $(1\,1\,\bar{2}0)$ plane normal to the tensile axis. Even propagation from small, blunt notches at high stresses failed to promote steps or coherent crack branching of these specimens. The fracture



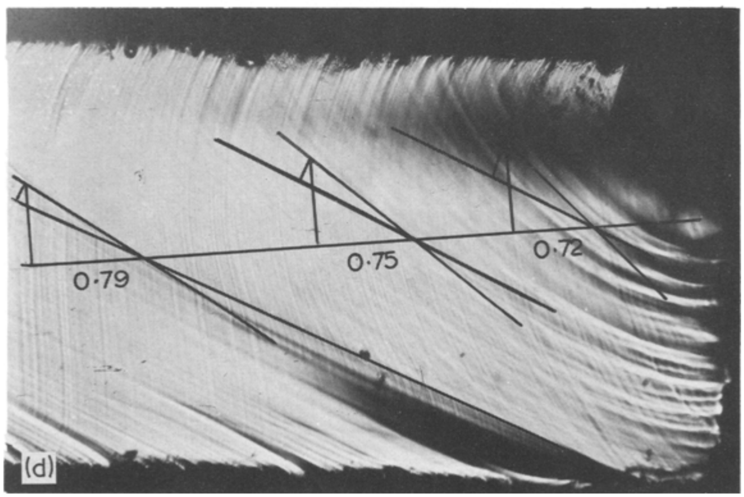


Figure 4 continued

surfaces are very like those of glass broken in tension in that they contain mirror and hackle regions. In addition, they display the Wallner lines (Fig. 4d) in the initial mirror regions which have been used to obtain fracture velocity data for this orientation. The $(1\,1\,\bar{2}0)$ fracture plane for this orientation is a flat maximum with regard to number of Si–O bonds per unit area [6] and has been reported as a very minor cleavage plane [18, 19]. The planar fracture normal to the applied stress and the glass-like behaviour of crystals of this orientation (E) must, therefore, be a consequence of the unsuitable orientation of the preferred rhombohedral cleavage planes with respect to the stress axis.

3.3 The velocity of fracture

The crack velocity, as obtained by the resistance grid method from a specimen of orientation E, is shown as a function of crack length c in Fig. 5. The solid line represents a least squares fit to the equation

$$V = V_{\mathrm{m}} + d_1 (c_0/c) + d_2 (c_0/c)^2 ,$$

where the constants V_{m}, d_1 and d_2 determine the shape of the curve and are such that the curve passed through the point ($c_0/c = 1$, $V = 0$). Fracture velocities obtained from an analysis of Wallner lines on the same specimen are also shown in this figure. The results of the two independent methods show an excellent agreement.

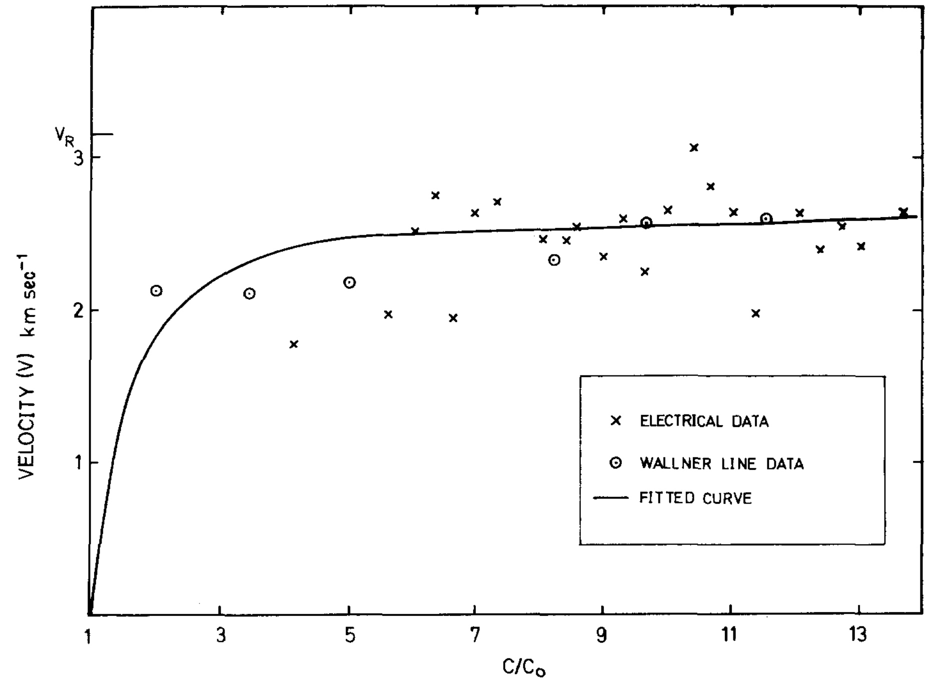


Figure 5 The velocity–distance relationship obtained by both the electrical method and an analysis of Wallner lines for a specimen of orientation E.

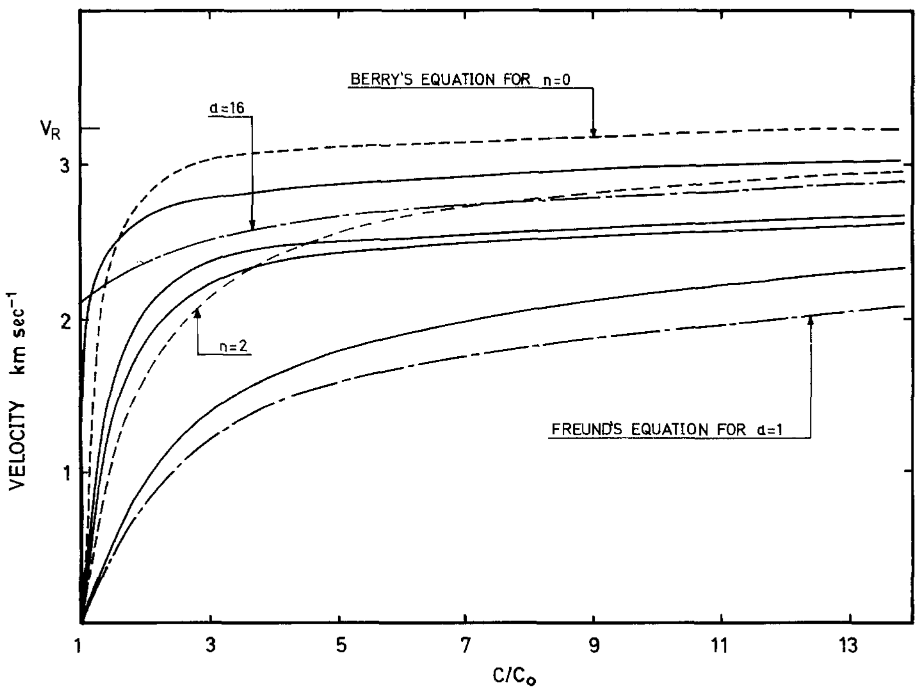


Figure 6 Experimental velocity–distance curves for four specimens of orientation E together with the curves predicted by the theories of Berry [20] and Freund [25].

Fig. 6 shows the smooth curves drawn through the data obtained by both experimental methods for four crystals of orientation E. The curves have the same form, but have different initial slopes corresponding to different accelerations. This difference can be explained by considering the sharpness of the tips of the initial notches. The applied tensile stress required to propagate an atomically sharp crack has a magnitude predicted by the Griffith theory. However, if the notch is blunt, a stress larger than the Griffith stress is required for fracture and thus the specimen acquires a greater amount of strain energy prior to crack propagation. This strain energy is released as surface and kinetic energies when fracture occurs in a brittle quartz crystal. Hence a crack, propagating from a blunt notch will have a greater acceleration than a crack propagating from a sharp notch and the terminal velocity will be approached within a shorter distance. Berry [20] formulated a theory which describes the velocity behaviour of a growing crack and also allows for the inclusion of an initial condition which describes the above effects when the fracture stress is greater than the Griffith stress σ_g. If we let

$$n = 2\sigma_g^2/\sigma_f^2$$

then Berry's equation is

$$V^2 = V_m^2(1 - c_0/c)(1 - \{n-1\}c_0/c).$$

This equation is plotted in Fig. 6 for the limiting values of n, namely $n = 0$ and $n = 2$, and the maximum crack velocity V_m is taken as that of Rayleigh surface waves V_R in the $[1\bar{1}00]$ direction in the $(11\bar{2}0)$ fracture plane for these specimens [21]. Various theories [22–24] for the propagation of high speed cracks in brittle solids predict an upper limit equal to the Rayleigh velocity but various experimental work suggests values of less than $0.7V_R$. The failure of the Berry equation to encompass our present experimental results may be due to an incorrect choice of V_m and to the assumptions inherent in the analysis. A more exact equation of motion of a semi-infinite crack under tensile loading is given by Freund [25] as

$$2\gamma = K_s^2(c)F(V)/E$$

where $K_s(c)$ is the static stress intensity factor for a crack of length c and $F(V)$ is a function of crack velocity V. Using the expression $\sigma_f\sqrt{(\pi c)}$ for the static stress intensity factor when an evenly distributed tensile stress σ_f is applied at $\pm\infty$ and the expression $(2E\gamma/\pi c_0)^{\frac{1}{2}}$ for the Griffith stress then Freund's equation becomes simply $c/c_0 = 1/F(V)$. For a blunt crack the fracture stress, σ_f is higher and letting $\alpha = \sigma_f^2/\sigma_g^2$, Freund's equation is $c/c_0 = 1/\alpha F(V)$. Our experimental values of fracture stress suggest that α is in the range 1 to 25 and the theoretical curves for $\alpha = 1$ and 16 are included in Fig. 4 for comparison with the experimental velocity curves.

4. Conclusions

(1) The stress required for the tensile fracture of quartz crystals is dependent upon the geometry of the initiating notch. Sharp notches introduced by thermal treatments give a value of approximately 2 J m^{-2} for the surface energy required for fracture at room temperature.

(2) The energy required for fracture shows a minimum at about 500 K.

(3) The presence of water reduces the stress required for fracture.

(4) Quartz shows a preference for cleavage along the rhombohedral planes. Fracture paths are influenced by static and dynamic stress fields.

(5) The velocity–distance curves show a form and a dependence upon fracture stress in the manner predicted by the theories of Berry [20] and Freund [25].

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References

1. R. D. BAËTA and K. H. G. ASHBEE, *Phil. Mag.* **22** (1970) 601.
2. A. C. MCLAREN and J. A. RETCHFORD, *Phys. Stat. Sol.* **33** (1969) 657.
3. R. D. BAËTA, J. W. HEAVENS and K. H. G. ASHBEE, European Conference on Electron Microscopy (1968) p. 507.
4. N. E. W. HARTLEY and T. R. WILSHAW, *J. Mater. Sci.* **8** (1973) 265.
5. M. V. SWAIN, J. S. WILLIAMS, B. R. LAWN and J. J. H. BEEK, *ibid* **8** (1973) 1153.
6. F. D. BLOSS and G. V. GIBBS, *Amer. Minerol.* **48** (1963) 821.
7. R. J. CHARLES, *J. Appl. Phys.* **29** (1958) 1549.
8. F. R. L. SCHOENING, Thesis, University of the Witwatersrand, South Africa (1959).
9. B. W. PAYNE and A. BALL, to be published.
10. J. E. FIELD, *Contemp. Phys.* **12** (1971) 1.

11. L. PAULING, "The Nature of the Chemical Bond" (Cornell Press, New York, 1960).
12. R. B. SOSMAN, "The Properties of Silica" (Chemical Catalog. Co., New York, 1927).
13. N. H. PETCH, "Fracture", Vol. 1, edited by H. Liebowitz (Academic Press, New York, 1968).
14. B. SCHWARTZ, *J. Amer. Ceram. Soc.* **35** (1952) 325.
15. S. S. BRENNER, *J. Appl. Phys.* **33** (1962) 33.
16. J. CONGLETON, N. J. PETCH and S. A. SHIELS, *Phil. Mag.* **19** (1969) 795.
17. J. J. GILMAN, *J. Appl. Phys.* **42** (1971) 3479.
18. S. K. ICHIKAWA, *Amer. J. Sci.* **189** (1915) 455.
19. J. L. ANDERSON, *Geol. Soc. Amer. Bull.* **53** (1945) 409.
20. J. P. BERRY, *J. Mech. Phys. Solids* 8 (1960) 194.
21. F. W. VOLTMER, E. P. IPPEN, R. M. WHITE, T. C. LIM and G. W. FARNELL, *Proc. IEEE* **56** (1968) 1634.
22. E. H. YOFFE, *Phil. Mag.* **42** (1951) 739.
23. K. B. BROBERG, *Arkiv. Fysik.* **18** (1960) 159.
24. J. W. CRAGGS, *J. Mech. Phys. Solids* 8 (1960) 66.
25. L. B. FREUND, *ibid* **20** (1972) 141.

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