$$\ln(S) = \ln(\alpha K_0) - Q'/RT \tag{6}$$

and

$$\ln(I.T^{1/2}) = \ln(Z.D_0) - \frac{Q}{2RT}$$

Plots of $\ln(S)$ and $\ln(I.T^{1/2})$ versus $1/T$ should be linear with slopes proportional to the activation energies for diffusion along and to the dislocation line, respectively. Fig. 2 illustrates these plots and from which

$$Q' = 0.3\,\text{eV}$$

and

$$Q = 0.6\,\text{eV}.$$

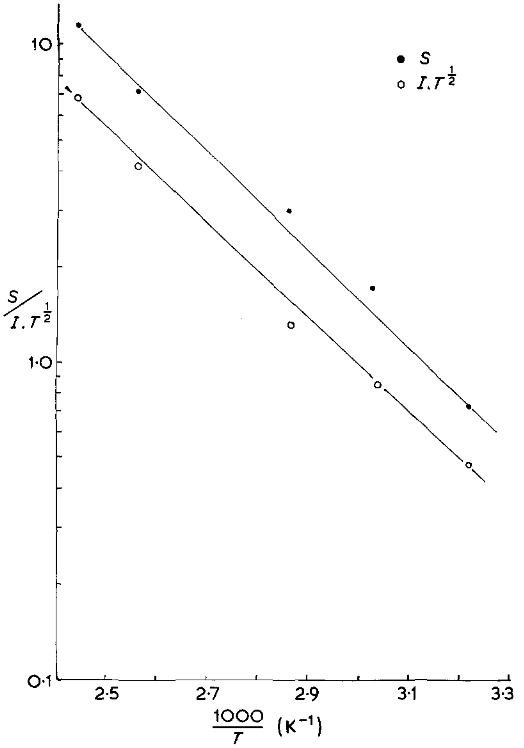


*Figure 2* Intercept times $T^{1/2}$ and slopes from Fig. 1. versus $T^{-1}$.

Thompson reports several papers in which a lattice energy and pipe diffusion energy of 0.64 and 0.4 eV, respectively, have been obtained.

The results obtained by Simpson and Sosin can, therefore, be explained in terms of the Granato–Lücke model of dislocation on damping. This has been achieved by modifying the Cottrell–Bilby equation to take into account the continuing production of point defects during irradiation. Pipe diffusion of the defect along the dislocation has also been included in the theory. From the results, the activation energies for diffusion to and along dislocations have been obtained and are in agreement with other workers.

## References

1. C. F. BURDETT and H. RAHMATALLA,
2. A. GRANATO and K. LUCKE, *J. Appl. Phys.* **27** (1956) 583.
3. H. M. SIMPSON, A. SOSIN and D. F. JOHNSTON *Phys. Rev.* **135** (1972) 1393.
4. G. J. DIENES, Ed, 'Studies in Radiation Effects in Solids" (Gordon and Breach, New York, 1969) p. 274.
5. J. FRIEDEL, "Dislocations" (Pergamon Press, Oxford, 1964).

*Received 18 October
and accepted 28 October 1976*

C. F. BURDETT
H. RAHMATALLA
*Department of Metallurgy,
University of Strathclyde,
Glasgow, UK*

---

## *Growth sector boundaries and their influence on quartz resonator performance*

The influence of crystal defects on quartz resonator performance has been the subject of some interest in the recent past [1, 2]. In the present paper, the occurrence of boundaries between regions having differences in their impurity incorporations contained in the central part of quartz reasonator plates is indentified with the malfunctioning of the crystals. These boundaries are thought to be growth sector boundaries (gsbs) [3–6] and growth cell boundaries [3].

The inclination of the plane of a quartz resonator plate relative to the crystallographic axes of the material is a sensitive function of its frequency–temperature behaviour [2]. The variation of the fractional change in frequency, $\Delta f/f$, with temperature for normally functioning AT-cut [7] resonators is shown in Fig. 1. This figure also

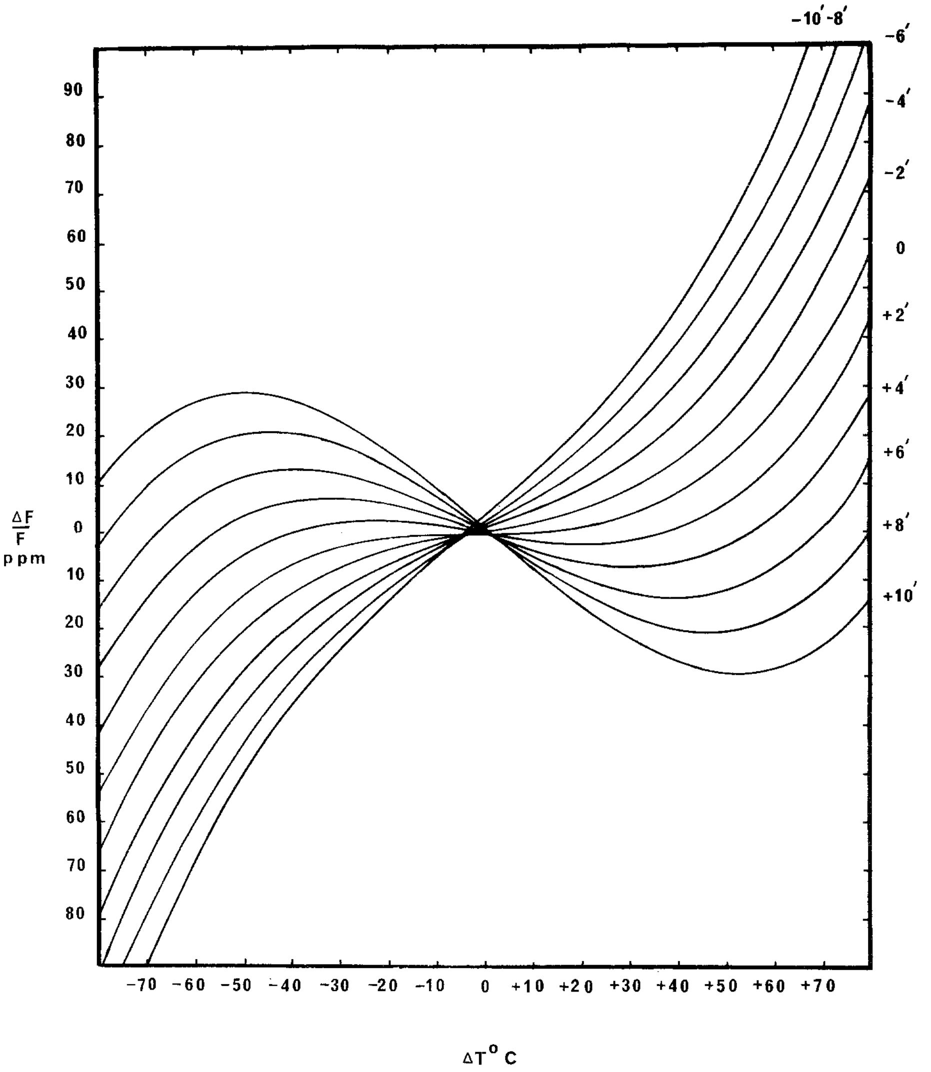


*Figure 1* The frequency–temperature characteristics for AT-cut resonators and for crystals whose planes are rotated from this exact orientation by small amounts about the *X*-axis of quartz, given in minutes on the right-hand ordinate. $\Delta T = 0$ represents 20° C.

indicates the frequency–temperature characterisics of resonators deviating from this exact orientation.

$\gamma$ or X-irradiation of quartz specimens containing $Al^{3+}$ impurities substituted for $Si^{4+}$ at the centre of the $SiO_4$ tetrahedron give rise to the formation of colour centres with their absorption peaks at 460 and 625 nm; the distribution of this type of impurity in the different sectors of growth for quartz grown by the conventional industrial process is known to generally follow a characteristic pattern [8]. Both X-ray topography [9] and the formation of colour centres by $\gamma$-irradiation have been used as means of defect identification in the present work.

Twenty 12 mm diameter resonator plates cut from Y-bar blocks of quartz were studied. Their planes lay within $\pm 4'$ of the exact AT-cut and their fundamental frequency mode for thickness shear vibrations [1] was at ~ 7 MHz. All the resonators had been previously found to exhibit an anomalously larger change in their fractional frequency with temperature (by a factor of ~ 3) than would be predicted by the family of curves shown in Fig. 1. The surface orientations of the resonators were measured to within $\pm \frac{1}{2}'$ by standard X-ray goniometric methods and their

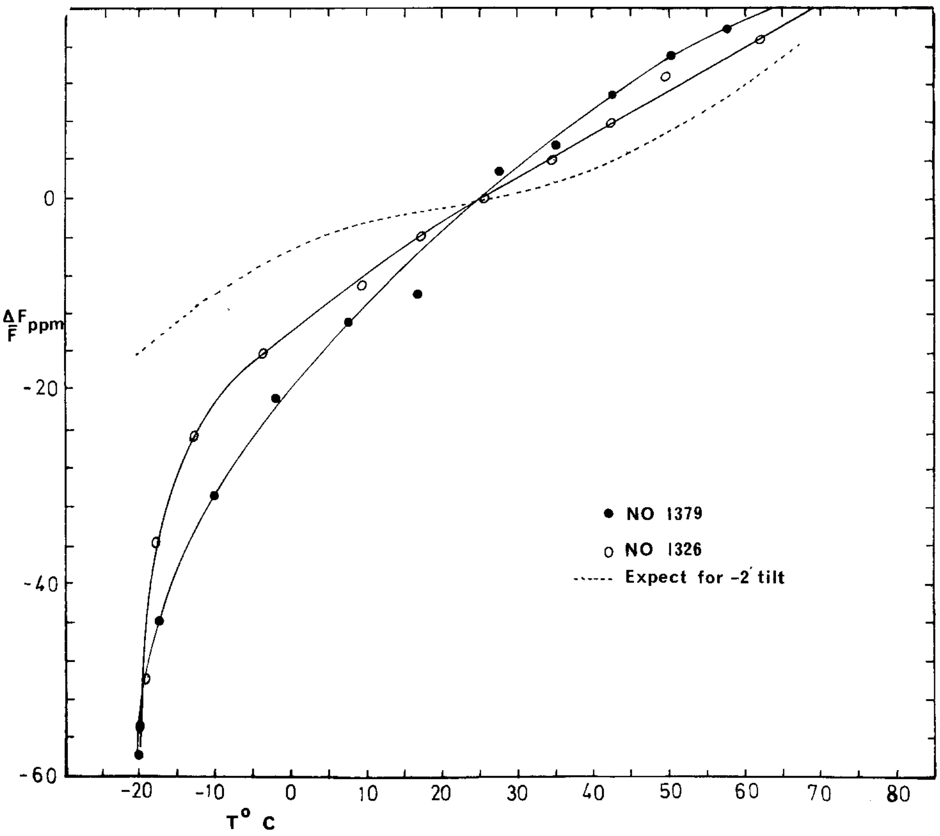
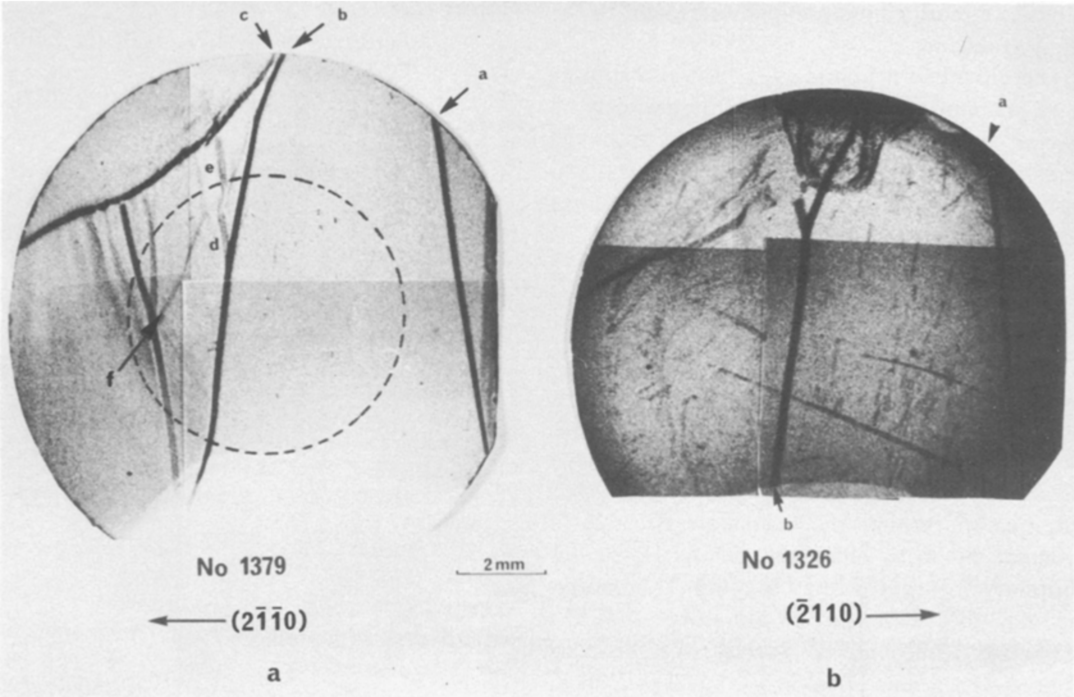


*Figure 2* The frequency–temperature characteristics for resonators no. 1379 and 1326. The dotted line represents the behaviour predicted by Fig. 1 for these crystals.

frequency-temperature characteristics between −20 and 60° C were also determined. The curves for two representative resonators is shown in Fig. 2 along with the predicted behaviour for normally functioning crystals; both resonators deviated from the exact AT-cut by −2′.

Following the frequency measurements, twelve of the twenty crystals were chosen at random for examination by X-ray topography and $\gamma$-irradiation. Fig. 3 a and b show Lang topographs of crystals no. 1379 and 1326 respectively, in which increased photographic blackening represents areas of higher X-ray fluxes. All twelve crystals showed one or more lines of enhanced intensity on their topographs in the region sandwiched by the evaporated metallic electrodes (represented by the dotted line in Fig. 3a). On Lang topographs of resonators showing no anomaly in their frequency–temperature behaviour, similar lines of enhanced intensity have sometimes been seen. However, they were found to lie either partly on the periphery of the region enclosed by the electrodes, or wholly outside it.

On comparing the sectorial pattern generally observed in Y-bar synthetic quartz [6, 8] (see Fig. 3c), with the dark lines on the topographs of the resonators, the lines of enhanced X-ray intensity were easily identified as being due to gsbs for ten of the twelve crystals. The pattern of colour centre formation induced by $\gamma$-irradiation confirmed this finding. For instance, in Fig. 3a, it is clear that the lines at a, b and c are due to the $-X/Z$, $Z/X$ and $s/{+}X$gsbs. The "flats" on the right-hand side of both crystals lie in the *Y*–*Z* plane of quartz and are inclined at an angle of ~ 35° to the *c*-axis. The faint lines at d and e are attributed to growth bands [10] and the contrast at f to the *x*/*s* gsb. The *Z*-growth region in this crystal is smaller and the *x* and *s* regions much larger than those generally encountered.



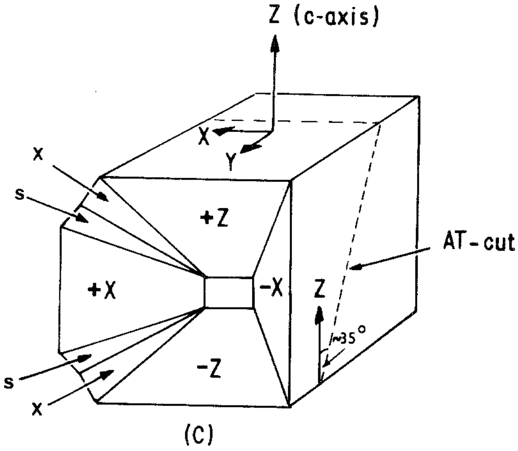


*Figure 3* Lang X-ray topographs of two malfunctioning resonators obtained using Mo$K\alpha_1$ radiation. Diffraction was from the $2\bar{1}\bar{1}0$ and $\bar{2}110$ planes for resonators (a) no. 1379 and (b) no. 1326. The arrows indicate the direction of the diffraction vectors, which lie on the plane of the page. The "flats" on the right-hand edges of the crystals lie in the $Y$–$Z$ planes of quartz and are inclined at an angle of $\sim 35°$ to the $Z$-axis. (c) A schematic representation of a Y-bar block of synthetic quartz illustrating the seed of rectangular section near the centre and the different growth sectors around it. The AT-cut is also indicated.

In the remaining two crystals, the line of enhanced intensity could not be identified unambiguously; the Lang topograph of one of them is shown in Fig. 3b. The straightness of line a and its angle of inclination to the $c$-axis suggests that it is due to a $-X/Z$ gsb. At first sight line b appears to be due to a $Z/x$ gsb. However, the absence of the image contrast from the $s/+X$ gsb in its vicinity casts doubt upon this interpretation. The pattern of colour centre formation did not clarify this ambiguity since material from some growth cells in the $Z$-region have been reported to colour on irradiation [11] and X-ray toporgaphic image contrast similar to that observed at gsbs has been seen at growth cell boundaries [3]. It is concluded that line b is either due to the boundary of a large growth cell in the $Z$-growth region, or it marks the boundary between the $Z$ and $+X$ sectors, with the $x$ and $s$ sectors not having formed in this crystal, or it may be due to the image contrast from the $Z/x$, $x/s$ and $s/+X$ gsbs superimposed.

The presence of gsbs contained in the volume of the crystal resonators between the electrodes, to which the vibrations are principally confined, appears to give rise to an anomalously large change in the frequency of the resonators with changes in temperature. This may be due either to the nature of the boundaries or simply because material of differing impurity incorporation is present in the vibrating reigion.

The growth cell boundary, which also appears to be an impurity boundary, and the gsb may be alike in structure judging qualitatively from the similarity in their X-ray topographical image contrast. However, the nature of the former has not yet been fully investigated.

A simple X-ray image converter capable of permitting the rapid detection of gsbs in quartz has recently been reported [12].

## Acknowledgements

The author is grateful to Mr J. Dowsett for discussions, the provision of the crystals examined and for laboratory facilities at Cathodeon Crystals Ltd, Cambridgeshire. His thanks are also due to Professor Sir N.F. Mott and Dr A. Howie for laboratory facilities at the Cavendish Laboratory, and to the Cavendish Laboratory and the Cambridge Philosophical Society for financial support. The Science Research Council is thanked for equipment grants.

## References

1. W. J. SPENCER, *Physical Accoustics* 5 (1968) 111.
2. D. B. FRASER, *ibid* 5 (1968) 59.
3. A. R. LANG and V. F. MIUSCOV, *J. Appl. Phys.* 38 (1967) 2477.
4. D. Y. PARPIA, *Phil. Mag.* 33 (1976) 715.
5. W. J. SPENCER and K. HARUTA, *J. Appl. Phys.* 37 (1967) 549.
6. M. TAKAGI, H. MINO and M. SATO, *J. Crystal Growth* 24, 25 (1974) 541.
7. W. J. CADY, "Piezoelectricity" (McGraw Hill, London, 1946).
8. A. J. COHEN, *J. Phys. Chem. Solids* 13 (1960) 321.
9. A. R. LANG *"Modern Diffraction and Imaging Techniques in Material Science"*, edited by S. Amelinckx, R. Gevers, G. Remant and J. van Landuyt (North-Holland, Amsterdam, 1969) p. 407.
10. U. BONSE, *Z. Phys.* 184 (1965) 71.
11. C. S. BROWN and L. A. THOMAS, *J. Phys. Chem. Solids* 13 (1960) 337.
12. D. Y. PARPIA and B. K. TANNER, *Phys. Stat. Sol.* (*a*) 6 (1971) 689.

*Received 25 October*
*and accepted 22 November 1976*

D. Y. PARPIA*
*Cavendish Laboratory,*
*Cambridge,*
*UK*

---

* Present address: School of Mathematical and Physical Sciences, University of Sussex, Brighton, UK.

---

## *Acoustic emission activity during accelerated conversion of high alumina cement pastes*

High alumina cement (HAC) owes its high initial strength to the formation of monocalcium aluminate decahydrate, dicalcium aluminate octahydrate and alumina gel, on hydration. These high strength aluminates are metastable, however, and decompose gradually to tricalcium aluminate hexahydrate and gibbsite (aluminium hydroxide) which are stable up to about 200° C. This process, termed "conversion", entails a crystallographic change from hexagonal to cubic and is accompanied by the evolution of water. Conversion takes place very slowly at normal ambient temperatures but is accelerated at higher temperatures. In recent years it has been established that under adverse conditions conversion leads to a serious loss of strength in HAC pastes and HAC concretes [1, 2]. The major factors affecting the strength loss during conversion are (a) the temperature of conversion, and (b) the water/cement ratio of the paste or concrete.

Pastes with a high water/cement ratio contain very little residual unhydrated cement. The water evolved during conversion, therefore, cannot be absorbed, and appears as free water in the interior of the paste. The main effect of increased temperature is to increase the conversion rate. This leads to a larger aluminate crystallite size, which is thought to adversely affect the strength.

Acoustic emissions (AE) are elastic stress waves generated within a material by rapid discontinuous relaxation of local stress. Common examples of processes emitting AE are (a) dislocation motion during plastic deformation of metals, (b) martensitic phase transformations and twinning, and (c) crack nucleation and propagation. It was not considered likely that the conversion process in HAC would itself be a source of acoustic emission, since the reaction proceeds continuously with