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Alexander Aning

Manfred Wuttig

*Missouri University of Science and Technology*

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## DYNAMICS OF TWINNING IN NATURAL $\alpha$ -QUARTZ†

ALEXANDER ANING and MANFRED WUTTIG

Department of Metallurgical Engineering, University of Missouri-Rolla, Rolla, MO 65401, U.S.A.

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**Abstract**—Finite amplitude internal friction experiments in  $\alpha$ -quartz are described and interpreted in terms of the theory of nonlinear anelasticity. The theory predicts a linear relationship between the driving force of the excitation and the period of the automodulation at its onset. This relation is substantiated by experiments performed with a natural  $\alpha$ -quartz reed vibrating in flexure at resonance frequencies between 65 and 170 Hz in the temperature range of 162° and 224°C. The data suggests that Dauphiné twinning in  $\alpha$ -quartz causes the automodulation governed by an activation energy of 92 kJ/mole. This activation energy characterizes short distance oxygen diffusion.

### 1. INTRODUCTION

The dynamics of defect motion can be investigated by internal friction studies.[1] Well known examples in the field of ceramics include the work on rutile by Wachman and Doyle[2] and internal friction studies on dislocation motion like the one in  $\alpha$ -quartz[3]. Most of these studies have been conducted at amplitudes of vibration very small when compared to one.

If studies are made at finite amplitudes, the internal friction due to dislocations changes along the general lines predicted theoretically by Granato and Lücker[3, 4]. In  $\alpha$ -quartz, however, internal friction maxima at harmonics occur which are larger than the fundamental peak, indicating a mechanism for energy dissipation which is characteristic of finite amplitudes of vibration[5]. This paper addresses itself to this phenomenon. It will be shown that the mechanism is twinning.

Twinning is known to occur at finite deformations or stresses. This is shown by the ideal stress-strain curve produced in Fig. 1[6] in which the coercive stress,  $\sigma_c$ , for the induction of mechanical or Dauphiné twinning in  $\alpha$ -quartz is indicated. Deformation reversal is achieved by switching domains to those of opposite orientation when the reverse coercive stress is reached or exceeded. Dauphiné twinning is demonstrated schematically in Fig. 2. In this figure the upper two unit cells represent one twin orientation, the lower

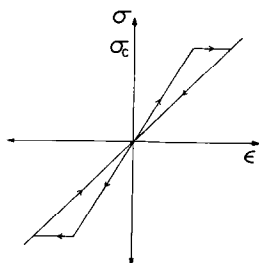


Fig. 1. The stress-strain curve of  $\alpha$ -quartz showing the coercive stress,  $\tau_c$ , required to induce Dauphiné twinning according to Ref.[6].

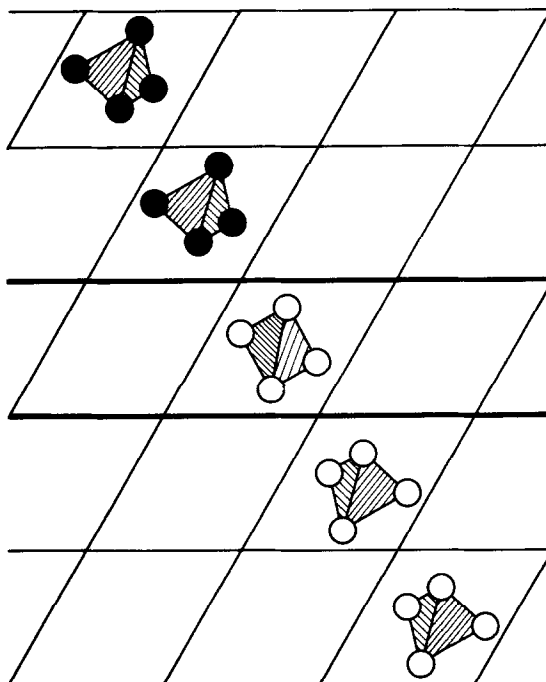


Fig. 2. Two Dauphiné twin related sections of  $\alpha$ -quartz. The two thick lines enclose the boundary unit cell layer with the structure of  $\beta$ -quartz. The two twins are characterized by the different orientation of selected oxygen tetrahedra in the center of a unit cell. The oxygen positions are marked by filled or open circles depending on the twin orientation.

two unit cells show the twinned configuration in which the orientations of the oxygen tetrahedra have been switched. The middle unit cell represents a domain wall with the structure of  $\beta$ -quartz[7]. For simplicity only the tetrahedron at the center of one unit cell in each layer is shown. Since twinning occurs at finite stresses a study of the dynamics of twinning must be conducted at finite amplitudes of deformation and the results interpreted in terms of the theory of nonlinear anelasticity previously developed by the authors[8]. The results of such a study will be presented below.

†Dedicated to Prof. H. Boersch on his 75th birthday.

2. NONLINEAR ANELASTICITY

The formal theory of internal friction at infinitesimal deformation amplitude—linear anelasticity—is long known [1,9]. The theory for finite deformation amplitudes—nonlinear anelasticity—has been developed more recently [8]. Its features salient to this study will therefore be presented first. The theory is an extension of the linear theory to finite amplitudes of vibration. The linear anelastic solid is characterized by

$$\sigma + \dot{\sigma}\tau = C_r\dot{\epsilon} + C_u\tau\dot{\epsilon}, \tag{1}$$

where  $C_r$  and  $C_u$  denote the relaxed and unrelaxed deformation parameters. Equation (1) is extended to the nonlinear case by considering  $C_r$  and  $C_u$  functions of the deformation, i.e.

$$\sigma + \dot{\sigma}\tau = C_r(\epsilon)\dot{\epsilon} + C_u(\epsilon)\tau\dot{\epsilon}. \tag{2}$$

For twinning, the functions  $C_r(\epsilon)$  and  $C_u(\epsilon)$  are most simply presented by fourth order polynomials.

The equation of motion of a nonlinear anelastic solid can be derived by combining eqn (2) with Newton's law,

$$\rho\partial^2\epsilon/\partial t^2 = \partial^2\sigma/\partial z^2, \tag{3}$$

where  $z$  is the spatial coordinate along the solid and  $\rho$  represents its density. A tractable equation for the traverse oscillation of a thin reed follows if the spatial dependence of the displacement is approximated by [10]

$$\epsilon(z, t) \approx x(t)[1 - \cos(\pi z/2l)], \tag{4}$$

where  $l$  is the length of the reed. The resulting differential equation for the amplitude of vibration  $x(t)$  is

$$\tau\ddot{x} + \ddot{x} + C_u(x)\dot{x}\omega_0^2\tau + \omega_0^2C_r(x)x = E \cdot \sin(\omega_1 t) \tag{5}$$

where  $\omega_0^2 = \pi^2 C_{r2}(4l^2\rho)^{-1}$ , and  $E \cdot \sin(\omega_1 t)$  is the excitation.

The solution of eqn (5) is of the form

$$x(t) = a(t) \cos[\omega_1 t + \theta(t)] \tag{6}$$

where the slowly varying functions  $a(t)$  and  $\theta(t)$  are solutions of the system of differential equations

$$\dot{a} = F(a, \theta), \tag{7}$$

and

$$\dot{\theta} = G(a, \theta). \tag{8}$$

The functions  $F$  and  $G$  have been evaluated [8]. The essential terms of both will be cited below. The system of differential eqns (7) and (8) admits to two kinds of solutions: The steady state solution for which

$\dot{a} = \dot{\theta} = 0$  yields the resonance characteristics of the reed made from a nonlinear anelastic solid. The general case  $\dot{a} \neq 0$  and  $\dot{\theta} \neq 0$  includes a special dynamical steady state in which  $a(t)$  and  $\theta(t)$  are periodic functions. In this case the forced vibration in eqn (6) is modulated. Since the modulation is not imposed by the external drive but rather a result of unusual properties of the nonlinear anelastic solid, it is referred to as automodulation. An example of an automodulation will be shown in the experimental section. Figure 3 shows a computed nonlinear resonance curve resembling the one obtained experimentally for the  $\alpha$ -quartz reed at constant excitation which will be shown below.

The condition for the occurrence of automodulation can be obtained by a series expansion of  $a(t)$  and  $\theta(t)$ . Expanding  $a(t)$  and  $\theta(t)$  around their steady state values  $a_0$  and  $\theta_0$ ,

$$a(t) = a_0 + \delta a(t), \quad \delta a/a_0 \ll 1, \tag{9}$$

and

$$\theta(t) = \theta_0 + \delta\theta(t), \quad \delta\theta/\theta_0 \ll 1, \tag{10}$$

it can be seen that  $\delta a$  is given by the differential equation

$$\delta\dot{a} - (F_a + G_\theta)\delta\dot{a} + (F_a G_\theta - G_a F_\theta)\delta a = 0, \tag{11}$$

where subscripts  $a$  and  $\theta$  in eqn (11) represent the respective partial differentials. Hence automodulation will set in when the damping term equals zero, i.e.

$$F_a = -G_\theta. \tag{12}$$

At the onset of automodulation only the terms linear in  $\epsilon$  of the functions  $C_u(\epsilon)$  and  $C_r(\epsilon)$  need be

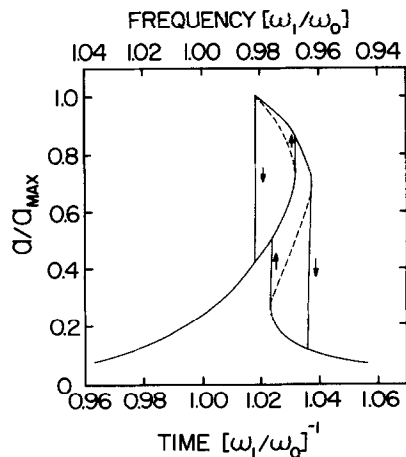


Fig. 3. Computer calculated nonlinear resonance curve after Ref. [8], resembling finite amplitude resonance curves obtained for the vibrating natural  $\alpha$ -quartz reed shown in Fig. 4. The dashed lines represent unstable portions and the arrows the jumps occurring as the frequency is tuned.

considered. This approximation simplifies the published functions  $F(a, \theta)$  and  $G(a, \theta)$ [8] for the unrelaxed case,  $\omega\tau \gg 1$ , as follows:

$$F(a, \theta) = (1 - \omega_1^2/\omega_0^2)a - 2(C_{u2} - 1)a - 4C_{u3}a^2 + 3C_{r3}a^2 + (2/\omega_0\tau)(C_{u2} - 1)b \sin \theta + 3(C_{u2} - 1)b \cos \theta, \quad (13)$$

and

$$G(a, \theta) = 3(1 - \omega_1^2/\omega_0^2) + 3(C_{u2} - 1) + 6C_{u3}a - 3(C_{u2} - 1)(b/a) \sin \theta + (2/\omega_0\tau)(C_{u2} - 1)(b/a) \cos \theta \quad (14)$$

where

$$b = E/(\omega_0^2 - \omega_1^2).$$

In eqns (13) and (14) the constants  $C_{u2}$  and  $C_{u3}$  are the second and third order unrelaxed deformation parameters and  $C_{r3}$  is the third order relaxed deformation parameter, all given in units the second order relaxed modulus,  $C_{r2}$ . The quantity  $b$  is amplitude of vibration. Through  $E$ , however, it is proportional to the driving force (see eqn 5). In the following it will therefore be referred to as the driving force. It will be shown below that the assumption  $\omega\tau \gg 1$  is justified. Using the threshold condition, eqn (12), an expression for the period of the automodulation,  $\tau_c$ , is derived as

$$\omega_{1c}\tau_c = (C_{u2} - 1)(b_c/a_c) \sin(\theta_c) / \{ (1 - \omega_{1c}^2/\omega_0^2) - (C_{u2} - 1)[2 + 3(b_c/a_c) \cos(\theta_c)] - 8C_{u3}a_c \}. \quad (15)$$

In eqn (15) the subscripts  $c$  denote critical values at the onset of the automodulation. Automodulation is a nonlinear phenomenon and hence the nonlinear term  $8C_{u3}a_c$  in eqn (15) is expected to dominate the linear contribution  $(C_{u2} - 1)[2 + 3(b_c/a_c) \cos(\theta_c)]$ . Since near resonance  $(1 - \omega_{1c}^2/\omega_0^2) \approx 0$  or  $\omega_{1c} \approx \omega_0$ , eqn (15) may be rewritten as

$$\omega_{1c}\tau_c \approx -(C_{u2} - 1)(b_c/a_c) \sin(\theta_c) / (8C_{u3}a_c) \quad (16)$$

revealing that the period of the automodulation at its onset, normalized by the critical period of the excitation of the vibration reed,  $\omega_{1c}^{-1}$ , depends linearly on the critical driving force,  $b_c$ . The negative sign on the right hand side renders  $\omega_{1c}\tau_c > 1$  since  $C_{u3} < 0$  for twinning[8].

### 3. EXPERIMENTAL PROCEDURE AND RESULTS

The experimental apparatus used in this study has been described before[8]. It has been constructed such that the driving force is proportional to the voltage driving the excitation. The specimen used for this study was a reed made out of natural Brazilian  $\alpha$ -quartz of the same origin as used for previous thermal expansion measurements[11]. Its plane was cut in a [210] direction, and the direction of vibration was [001]. The reed's dimensions were 2.4 cm by

0.5 cm by 0.06 cm. Measurements were made between 162° and 224°C. In this temperature range the resonance frequency of the flexural vibrations varied from about 65 Hz at the higher temperature to 170 Hz at the lower end of the temperature range. The experiments were performed in such a way that at the onset of automodulation, the critical driving frequency,  $\omega_{1c}$ , is almost equal to the resonance frequency  $\omega_0$ . Hence these two frequencies will be used interchangeably in the discussion.

Figure 4 shows a series of resonance curves taken with an  $x$ - $y$  recorder at four driving forces at the constant temperature of 224°C. At this temperature, the critical driving force required to produce the automodulation has a voltage equivalence of 0.0125 V. The aforementioned example of the automodulation is shown for the amplitude at the top, left corner of Fig. 4. It can be seen how the amplitude of oscillation of the reed oscillating with a frequency of 65 Hz varied slowly as function of time, i.e. it was automodulated. It should also be seen that the automodulation frequency was about 3 Hz in this particular case.

### 4. DISCUSSION

The results shown in Fig. 4 can be interpreted and analyzed in terms of the theory of nonlinear anelasticity. The nonlinear resonance curve on the right side of Fig. 4 has the same features as the theoretically calculated one presented in Fig. 3. It is also clear from the experiment that until a critical driving force or amplitude is reached, no automodulation is observed: In the example in Fig. 4, the automodulation sets in at driving voltage of  $U_d = 0.0125$  V. The critical driving voltage at which the automodulation sets in and its corresponding frequency,  $\tau_c^{-1}$ , are both temperature dependent, as will be discussed in more detail below.

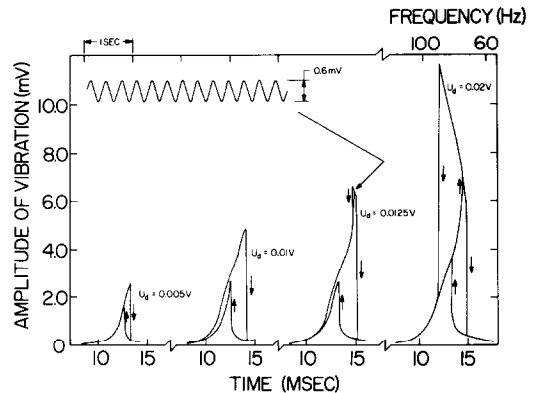


Fig. 4. A series of experimental resonance curves and an example of an automodulation of natural  $\alpha$ -quartz reeds at 224°C. The curves are copies of chart recordings of a voltage proportional to the amplitude of vibration as a function of the period of oscillation (resonance curves, lower abscissa) and time (automodulation, upper left abscissa). The automodulation was recorded at the critical drive voltage  $U_d = 0.0125$  V and the period of oscillation indicated by the arrows.

The Arrhenius relation for the frequency,  $\tau_c^{-1}$ , is given by

$$\tau_c = \tau_{c0} \exp(Q/RT), \quad (17)$$

where  $R$  is the gas constant and  $Q$  is the activation energy characteristic of the relaxation mechanism. Since the normalized time is proportional to the critical driving force,  $b_c$ , (see eqn 16) applied to the nonlinear anelastic reed, and  $U_c \propto b_c$ , eqn (17) may be rewritten as

$$\ln U_c = \ln k + Q/RT, \quad (18)$$

where various proportionality constants have been contracted into  $k$ . The quantity  $U_c$  is the critical driving voltage normalized to the critical driving voltage at a selected reference temperature. The Arrhenius plot for  $U_c$  is shown in Fig. 5. The least square analysis for this plot yields

$$\ln U_c = -25 + 91.2 \text{ kJ}/RT. \quad (19)$$

Figure 5 also shows the Arrhenius plot for the normalized automodulation frequency  $(\omega_0\tau_c)^{-1}$  whose equation is represented by

$$\ln(\omega_0\tau_c) = -19.7 + 93.7 \text{ kJ}/RT. \quad (20)$$

It is evident that both Arrhenius expressions, eqn (19) and (20), have approximately the same activation energy. This does suggest that the period of the automodulation is the same as the relaxation time of the defect mechanism giving rise to it. It also follows from eqn (20) that in the temperature range covered by this study  $10 \leq \omega_0\tau_c \leq 400$ . The assumption  $\omega_0\tau \gg 1$  made in the course of the derivation of eqn (16) is then self consistent with the results.

The experimental results demonstrate that the automodulation is controlled by a thermally activated process. This process is triggered only at finite amplitudes of vibration, and occurs above a critical driving

force,  $b_c$ , with a period,  $\tau_c$ . On the basis of the theory of nonlinear elasticity it was shown that  $\omega_0\tau_c \propto b_c$ . Hence it must be expected both  $\omega_0\tau_c$  and  $b_c$  obey the same Arrhenius relation. This is indeed so. The microscopic process giving rise to the automodulation must therefore be one which, first, occurs only at finite amplitudes of oscillation. It must, second, be one characterized by an asymmetrical deformation potential since the experimentally observed relationship  $\omega_0\tau_c \propto b_c$  (see Fig. 5) confirms eqn (16) based on such a potential. Both criteria are fulfilled if it is assumed that twinning is responsible for the reported observations[8]. Since it is known that Dauphiné twinning can be readily induced mechanically[6] it is suggested that Dauphiné twinning is responsible for the automodulation. The observed average activation energy of 92 kJ/mole then represents the activation energy of the reorientation of the oxygen tetrahedra from one configuration of the untwinned state to the configuration of the twinned state as shown in Fig. 2. This reorientation must occur by the motion of oxygen atoms. The activation energy of automodulation thus represents the activation energy of oxygen motion from one crystallographic site represented by open circles. This motion qualitatively resembles interstitial diffusion since the open circle oxygen positions become "available" as the twin boundary sweeps past the appropriate tetrahedron upon deformation by twinning. The observed activation energy characterizing the automodulation should thus be significantly smaller than the activation energy of long range oxygen diffusion in  $\alpha$ -quartz listed in Table 1. While no diffusion data of oxygen diffusion in  $\alpha$ -quartz in the temperature range of this study could be found, it can be seen that the activation energy for twinning measured here is at least a factor of two smaller than the listed values in qualitative agreement with the interstitial type short range oxygen diffusion. It is further noted that the activation energy of the present study agrees with previously published[5] but not positively identified data as can be seen from Fig. 5.

## 5. CONCLUSION

This study has revealed that finite amplitude flexural vibrations in natural  $\alpha$ -quartz can be described by the theory of nonlinear anelasticity. The theoretical prediction of the linear relationship between the critical driving force,  $b_c$ , and the critical

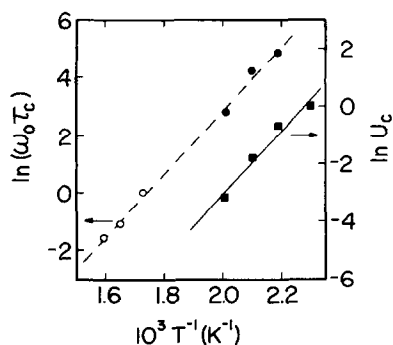


Fig. 5. Arrhenius plots for the normalized period of the automodulation,  $\omega_0\tau_c$ , and the normalized driving voltage,  $U_c$ , at the onset of the automodulation. The value,  $U_c$ , has been normalized to the critical driving voltage at 162°C. The open circles represent earlier data[5].

Table 1. Activation energies for oxygen diffusion in  $\alpha$ -quartz

Activation Energy (kJ/Mole)	Temperature (°C)	Reference
301	20-80	12
197	870-1180	13
218	1010-1220	14

period of the automodulation at its onset,  $\omega_0\tau_c$ , was substantiated by the experiment. The main result of this study is that the automodulation phenomenon does represent the mechanism of Dauphiné twinning in natural  $\alpha$ -quartz governed by an activation energy of 92 kJ/mole.

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